Supplementary material for:

Pseudallicins A-D, Four Complex Ovalicin Derivatives from *Pseudallescheria boydii* SNB-CN85

Jonathan Sorres,† Charlotte Nirma,† Véronique Eparvier,*,† Didier Stien*,‡

†CNRS, Institut de Chimie des Substances Naturelles UPR2301, Université Paris-Saclay, 91198 Gif-sur-Yvette, France.

‡Sorbonne Universités, UPMC Univ Paris 06, CNRS, Laboratoire de Biodiversité et Biotechnologies Microbiennes (LBBM), Observatoire Océanologique, Banyuls-sur-Mer, France.

Table of Contents

List of Tables

Table of Figures

1. Experimental

1.1. General experimental procedures

Optical rotations ($[\alpha]_D$) were measured on an Anton Paar MCP 300 polarimeter in a 100 mm long 350 µL cell. IR spectra were recorded using a Perkin Elmer Spectrometer BX FT-IR. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 600 MHz spectrometer equipped with 3 mm inverse detection cryoprobe or a Bruker 500 MHz spectrometer equipped with a 5 mm inverse detection probe. Chemical shifts (δ) are reported as ppm based on TMS signal. HRESIMS measurements were performed using a Waters Acquity UPLC system with column bypass coupled to a Waters Micromass LCT Premier time-of-flight mass spectrometer equipped with an electrospray interface (ESI). Flash chromatography was performed on a Grace Reveleris system with dual UV and ELSD detection equipped with a 40 g C_{18} column. Analytical and preparative HPLCs were conducted with a Gilson system equipped with a 322 pumping device, a GX-271 fraction collector, a 171 diode array detector, and a prepELSII electrospray nebulizer detector. Columns used for these experiments included a Phenomenex Luna C18 5 µm 4.6 × 250 mm analytical column and a Phenomenex Luna C18 5 µm 21.2 × 250 mm preparative column. The flow rate was set to 1 or 21 mL/min, respectively, using a linear gradient of H_2O mixed with an increasing proportion of CH_3CN. Both solvents were HPLC grade, modified with 0.1%

formic acid. Potato dextrose agar (PDA) was purchased from Fluka Analytical. Molecular analyses were performed externally by BACTUP, France.

1.2. Collection and identification of *Pseudallescheria boydii* SNB-CN85

A termite worker was collected from an aerial termite nest located in Rémire-Montjoly, French Guiana, in July 2011. The termite was identified as *Termes* cf. *hispaniolae* by Prof. Reginaldo Constantino (University of Brasilia, Brazil). The worker was surface-sterilized by successive soakings in 70% EtOH (2 min), 5% NaOCl (2 min), and sterile water. The termite was subsequently placed in a Petri dish containing a solid PDA medium. After 1 week at 25 °C, the first fungal hyphae to emerge from the insect were sampled and transferred into other Petri dishes. One of the microbial colony consisted in a pure fungus, which was saved in triplicate at −80 °C in H_2O−glycerol (50/50). A sample was submitted for amplification of the nuclear ribosomal internal transcribed spacer region ITS. Sequencing allowed for strain identification by NCBI sequence comparison (Blastn®). The sequence has been registered in the NCBI GenBank database (http://www.ncbi.nlm.nih.gov) under the registry number KJ023743.

1.3. Large-scale cultivation and fractionation of *Pseudallescheria boydii* SNB-CN85

The *P. boydii* strain was cultivated on PDA at 26 °C for 15 days, initially on a small scale and then on 150 14-cm Petri dishes. The fungus and culture medium were then transferred into a large container and macerated with EtOAc for 24 h. The organic solvent was then collected by filtration, washed with H_2O in a separatory funnel, and evaporated, yielding 3.57 g extract. A portion of the extract (1.13 g) was subjected to a reverse phase flash chromatography using a gradient of H_2O mixed with an increasing proportion of CH_3CN to afford 6 fractions (A to E). The column was then eluted with a CH_3CN:CH_2Cl_2 (1:1) mixture. Fraction D (300 mg, eluted with H_2O:CH_3CN, 2:8) was purified by reverse phase flash chromatography using the same solvents system as mentioned above, with a modified gradient. The major compound was collected in pure form and was identified as ovalicin (**1**) (28.1 mg). Fraction E (80 mg, eluted with H_2O:CH_3CN, 1:1) was subjected to a preparative HPLC (elution gradient from 25:75 to 10:90 over 30 min) to afford 5-hydroxy-8-acetoxy-

trans-bergamotene (**2**) (2.2 mg, RT = 8.7 min), pseudallicin A (**3**) (1.1 mg, RT = 13.2 min), pseudallicin B (**4**) (1.0 mg, RT = 14.3 min), pseudallicin C (**5**) (1.1 mg, RT = 29.5 min) and pseudallicin D (**6**) (0.7 mg, RT = 32.7 min).

Ovalicin (1): White powder; $[\alpha]^{22}_{D}$ –55.7 (*c* 0.14, MeOH) / –77.7 (*c* 0.13 $CDCl_3$); ^1H NMR (500 MHz, $CDCl_3$) see Table S1.

5-hydroxy-8-acetoxy-*trans*-bergamotene (2): Amorphous solid; $[\alpha]^{22}_{D}$ –1.3 (*c* 0.16, MeOH); IR ν_{max} 3442, 2955, 1713, 1374, 1259 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) see Table S2; ^{13}C NMR (125 MHz, CD_3OD) see Table S2; HRESIMS *m/z* 301.1783 $[M+Na]^+$ (calcd. for $C_{17}H_{26}O_3{}^{23}Na$, 301.1774).

Pseudallicin A (3): Amorphous solid; $[\alpha]^{22}_{D}$ –16,0 (*c* 0.05, MeOH); ^1H NMR (500 MHz, CD_3OD) see Tables 1 and S4; ^{13}C NMR (125 MHz, CD_3OD) see Tables 1 and S4; HRESIMS *m/z* 603.3541 $[M + H]^+$ (calcd for $C_{34}H_{51}0_9$, 603.3528).

Pseudallicin B (4): Amorphous solid; $[\alpha]^{22}_{D}$ –48,0 (*c* 0.05, MeOH); ^1H NMR (500 MHz, CD_3OD) see Tables 1 and S5; ^{13}C NMR (125 MHz, CD_3OD) see Tables 1 and S5; HRESIMS *m/z* 603.3554 $[M + H]^+$ (calcd for $C_{34}H_{51}0_9$, 603.3528).

Pseudallicin C (5): Amorphous solid; $[\alpha]^{22}_{D}$ –10,0 (*c* 0.01, MeOH); ^1H NMR (500 MHz, CD_3OD) see Tables 1 and S7; ^{13}C NMR (125 MHz, CD_3OD) see Tables 1 and S7; HRESIMS *m/z* 620.4313 $[M + H]^+$ (calcd for $C_{39}H_{58}N0_5$, 620.4310).

Pseudallicin D (6): Amorphous solid; $[\alpha]^{22}_{D}$ +30,0 (*c* 0.01, MeOH); ^1H NMR (500 MHz, CD_3OD) see Tables 1 and S8; ^{13}C NMR (125 MHz, CD_3OD) see Tables 1 and S8; HRESIMS *m/z* 620.4315 $[M + H]^+$ (calcd for $C_{39}H_{58}N0_5$, 620.4310).

1.4. Hydrolysis of 5-hydroxy-8-acetoxy-*trans*-bergamotene (2)

Compound **2** (0.9 mg, 3.23 μmol) was dissolved in THF (700 μL). LiOH (1.2 mg, 50.0 μmol) and distilled water (20 μL) were added and the mixture was stirred for 90 min at 60 °C. The solution was concentrated under reduced pressure and the residue was dissolved in distilled water (700 μL). The aqueous solution was extracted with Et_2O (3 × 0.5 mL). The combined organic layers were washed with water (2 mL), filtered and evaporated to afford 5,8-dihydroxy-*trans*-bergamotene (0.2 mg, 0.85 μmol, 25 %).

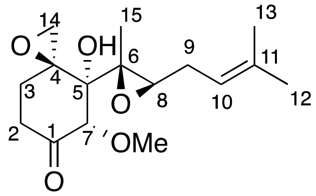
5,8-dihydroxy-*trans*-bergamotene: $[\alpha]^{22}_{D}$ –7.0 (*c* 0.06, MeOH); ^1H NMR (500 MHz, $CDCl_3$) see Table S3.

1.5. Preparation of the *(R)*- and *(S)*-MTPA esters of pseudallicin C (4)

Two portions of compound **4** (0.1 mg) were treated overnight with with *(S)*-(+)- and *(R)*-(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (1 µL) in $CDCl_3$ (0.25 mL)/C_5D_5N (1 µL) at room temperature to afford the *(R)*- and *(S)*-MTPA esters, respectively.

***(R)*- and *(S)*-MTPA Esters of pseudallicin C (4)**: ^{1}H NMR (600 MHz, CD_3OD), see diagnostic signals Table S6.

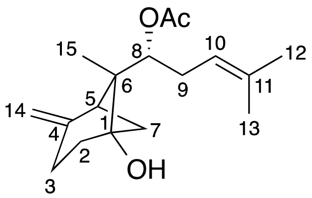
Table S1. NMR data table for ovalicin (**1**) and comparison with literature data



	Experimental	Literature[1]
Position	δ_H (*J* in Hz)[a]	δ_H (*J* in Hz)[b]
1		
2	a: 2.71, dddd (14.0, 12.1, 6.7, 0.9)	a: 2.62, ddd (12.5, 7.3, 6.7)
	b: 2.37, ddd (14.0, 5.6, 3.2)	b: 2.27, m
3	a: 2.48, ddd (13.6, 12.1, 5.6)	a: 2.41, dd (13.2, 5.3)
	b: 1.52, ddd (13.6, 6.8, 3.2)	b: 1.42, ddd (13.2, 7.3, 2.3)
4		
5		
6		
7	4.36, d (0.9)	4.27, d (0.7)
8	2.90, t (6.5)	2.80, t (6.5)
9	a: 2.35, m	2.27, m
	b: 2.20, m	2.10, ddd (14.5, 7.3, 2.0)
10	5.23, m	5.13, tq (7.3, 1.3)
11		
12	1.75, d (0.9)	1.66, s
13	1.67, brs	1.58, s
14	a: 3.07, d (4.4)	a: 2.97, d (4.3)
	b: 2.72, d (4.4)	b: 2.63, d (4.3)
15	1.36, s	1.26, s
OCH_3	3.49, s	3.39, s

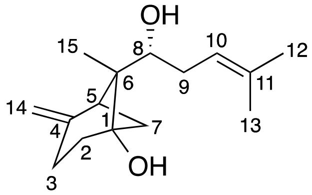
(a) ^{1}H NMR data recorded in CD_3OD at 500 MHz. (b) ^{1}H NMR data recorded in CD_3OD at 270 MHz.

Table S2. Full NMR data table for 5-hydroxy-8-acetoxy-*trans*-bergamotene (**2**)



Position	δ_C, type	δ_H (*J* in Hz)	COSY	HMBC	NOESY
1	76.1, C				
2	32.4, CH_2	a: 1.96, m	2a, 3a, 3b	1, 7	2a, 3b
		b: 1.72, ddd (12.8, 11.5, 1.7)	2b, 3a, 3b	1, 3, 4, 6, 7	2b, 3a
3	25.7, CH_2	a: 2.64, m	2a, 3b	2, 4	2a, 3b, 7b
		b: 2.34, m	2b, 3a	1, 4	3a
4	149.8, C				
5	44.0, CH	2.52, d (6.8)	7a	1, 3, 4, 6, 8, 14	14b, 9
6	53.8, C				
7	36.1, CH_2	a: 2.37, m	5, 7b	1, 2, 4, 5	7b, 8
		b: 1.82, d (10.0)	7a	1, 2, 4, 5, 6, 15	3a
8	76.0, CH	5.59, dd (8.7, 4.1)	9	6, 9, 10, 15, CO	5, 7a, 9
9	36.5, CH_2	2.28, m	8, 10	10, 11	5, 8, 10
10	122.0, CH	5.16, m	9, 12, 13	9, 12, 13	12
11	134.7, C				
12	26.1, CH_3	1.69, brs	10	10, 11, 13	10
13	18.0, CH_3	1.64, brs	10	10, 11, 13	9
14	108.5, CH	a: 4.70, m	14b	3, 5	3b
		b: 4.64, m	14a	3, 4, 5	5
15	12.4, CH_3	0.92, s		1, 5, 6, 8	2b, 9
H_3C-CO	21.6, CH_3	1.96, s		CO	
CO	173.2, C				

Table S3. NMR data table for 5,8-dihydroxy-*trans*-bergamotene and comparison with literature data



	Experimental	Literature[2]		Literature[3]	
Position	**δ_H (*J* in Hz)**[a]	**δ_C, type**[b]	**δ_H (*J* in Hz)**[a]	**δ_C, type**[c]	**δ_H (*J* in Hz)**[a]
1		77.4, C		76.6, C	
2	a: 1.94, m	32.2, CH_2	a: 1.94, m	31.5, CH_2	a: 1.94, m
	b: 1.80, ddd (12.7, 11.1, 1.7)		b: 1.76, dt (18.5, 9.5)		b: 1.80, brt (12.3)
3	a: 2.60, m	26.2, CH_2	a: 2.62, m	25.2, CH_2	a: 2.61, ddd (10.9, 7.3, 2.6)
	b: 2.34, m		b: 2.33, dd (18.5, 9.5)		b: 2.33, brd (10.9)
4		149.7, C		148.0, C	
5	2.36, d (6.6)	43.5, CH	2.41, ddd (10.0, 7.0, 1.5)	42.1, CH	2.36, d (6.8)
6		53.2, C		52.4, C	
7	a: 2.41, ddd (9.8, 7.0, 2.5)	36.6, CH_2	a: 2.46, d (7.0)	36.4, CH_2	a: 2.41, ddd (9.8, 6.8, 2.1)
	b: 1.84, d (9.8)		b: 1.85, d (10.0)		b: 1.89, d (9.8)
8	4.30, dd (9.8, 2.5)	75.9, CH	4.32, dd (6.5, 5.5)	74.3, CH	4.30, dd (10.0, 2.5)
9	a: 2.20, m	32.1, CH_2	2.11, m	31.2, CH_2	a: 2.20, m
	b: 2.04, m				b: 2.05, m
10	5.23, m	123.1, CH	5.29, dt (8.0, 1.0)	121.0, CH	5.23, brt (7.3)
11		133.7, C		135.2, C	
12	1.74, brs	26.0, CH_3	1.72, brs	25.9, CH_3	1.74, brs
13	1.65, brs	18.0, CH_3	1.64, brs	18.0, CH_3	1.65, brs
14	a: 4.68, m	107.9, CH	a: 4.66, dd (1.5, 1.0)	107.7, CH	a: 4.68, brs
	b: 4.60, m		b: 4.59, d (1.5)		b: 4.60, brs
15	0.83, s	11.0, CH_3	0.82, s	10.5, CH_3	0.84, s

(a) ^{1}H NMR data recorded in $CDCl_3$ at 500 MHz. (b) ^{13}C NMR data recorded in $CDCl_3$ at 100 MHz; (c) ^{13}C NMR data recorded in $CDCl_3$ at 125 MHz.

Table S4. Full NMR data table for pseudallicin A (**3**) and comparison with the ^{13}C spectrum of ovalicin (**1**)

	Literature[1]	**Experimental**				
position	**Ovalicin δ_C, type**	**δ_C, type**	**δ_H (*J* in Hz)**	**COSY**	**HMBC**	**NOESY**
1		175.4, C				
2		69.9, CH	4.40, dd (8.4, 4.0)	3a, 3b	1, 3, 4	3a, 3b, 5a, 5b
3		44.6, CH_2	a: 2.21, dd (14.4, 4.0)	2, 3b	1, 2, 4, 5, 11	2, 3b
			b: 2.00, dd (14.4, 8.4)	2, 3a	1, 2, 4, 5, 11	2, 3a, 5a
4		84.4, C				
5		37.8, CH_2	a: 1.78, m	5b, 6a, 6b, 11a		2, 3b, 5b, 6a, 14
			b: 1.61, m	5a, 6a, 6b		2, 5a, 6b
6		29.4, CH_2	a: 2.47, m	5a, 5b, 6b, 12a, 12b		5a, 6b, 13, 14
			b: 2.16, m	5a, 5b, 6a, 12a, 12b	4, 5, 8, 7, 12	5b, 6a, 12b
7		150.0, C				
8		55.7, CH	2.70, brd (5.0)	11a, 11b	4, 7, 12, 19	11a, 11b, 12, 13, 19
9		86.4, C				
11		43.4, CH_2	a: 2.46, ddd (11.8, 5.0, 2.7)	5a, 8, 11b		8, 11b, 19
			b: 1.685, m	8, 11a	7, 8, 9	8, 11a
12		109.1, CH_2	a: 4.65, t (2.4)	6a, 6b	6, 8	8
			b: 4.62, t (2.1)	6a, 6b	6, 8	6b
13		134.6, CH	5.67, d (15.4)	14	9, 15	6a, 8, 15, 19
14		126.0, CH	6.49, dd (15.4, 10.9)	13, 15, 18	9, 15	5a, 6a, 17, 19
15		126.3, CH	5.73, brd (10.9)	14, 17		13, 18
16		135.2, C				
17		18.5, CH_3	1.745, s	15	15, 16, 18	14
18		26.2, CH_3	1.752, s		15, 16, 17	15
19		29.8, CH_3	1.29, s		8, 9, 13	8, 11a, 13, 14
1'	80.0, C	82.8, C				
2'	87.7, CH	86.1, CH	4.69, brs	4'a	1', 3', 16'	4'a, 15', 16'
3'	209.4, C	211.2, C				
4'	37.6, CH_2	36.6, CH_2	a: 2.76, brtd (13.5, 7.4)	2', 4'b, 5'a, 5'b	3', 5'	2', 4'b
			b: 2.24, m	4'a, 5'a, 5'b	3'	4'a, 5'a, 5'b
5'	31.4, CH_2	32.7, CH_2	a: 2.13, td (13.7, 5.0)	4'a, 4'b	1', 3', 6'	4'b, 14'b
			b: 2.06, m	4'a, 4'b	1', 3', 6'	4'b, 14'b
6'	62.2, C	76.5, C				
7'	61.9, C	62.5, C				
8'	58.2, CH	58.2, CH	2.97, t (6.5)	9'a, 9'b, 15'	9', 10'	9'a, 9'b, 10', 14'a, 14'b
9'	28.4, CH_2	28.3, CH_2	a: 2.39, m	8', 9'b, 10'	7', 8', 10', 11'	8', 9'b, 10', 12', 15'
			b: 2.27, m	8', 9'a, 10'	8', 10', 11'	8', 9'a, 10', 12', 15'
10'	120.0, CH	119.7, CH	5.28, t hept (7.6, 1.5)	9'a, 9'b, 12', 13'	12', 13'	8', 9'a, 9'b, 13', 14'a
11'	136.4, C	136.2, C				
12'	18.4, CH_3	18.3, CH_3	1.684, brs	10'	10', 11', 13'	9'a, 9'b
13'	26.2, CH_3	26.1, CH_3	1.735, brs	10'	10', 11', 12'	10'
14'	52.0, CH_2	70.2, CH_2	a: 4.27, brd (10.9)	14'b	1, 5', 6'	8', 10', 14'b, 15'
			b: 4.16, d (10.9)	14'a	1, 5'	5'a, 5'b, 8', 14'a
15'	15.3, CH_3	16.3, CH_3	1.55, s	8'	1', 7', 8'	2', 9'a, 9'b, 14'a, 16'
16'	59.6, CH_3	59.7, CH_3	3.49, s		2'	2', 15'

Table S5. Full NMR data table for pseudallicin B (**4**) and comparison with the ^{13}C spectrum of ovalicin (**1**)

	Literature[1]	Experimental				
position	Ovalicin δ_C, type	δ_C, type	δ_H (*J* in Hz)	COSY	HMBC	NOESY
1		175.7, C				
2		69.9, CH	4.39, dd (8.8, 4.2)	3a, 3b	1, 3, 4	3a, 3b, 5a, 5b
3		45.5, CH_2	a: 2.26, dd (14.2, 4.2)	2, 3b	1, 2, 4, 5, 11	2, 3b
			b: 2.01, dd (14.2, 8.8)	2, 3a	1, 2, 4, 5, 11	2, 3a, 5b
4		84.3, C				
5		36.3, CH_2	a: 1.92, m	5b, 6a, 6b, 11a	7, 11	2, 5b, 6a
			b: 1.64, ddd (12.6, 10.7, 6.8)	5a, 6a, 6b		2, 3b, 5a, 6b
6		29.4, CH_2	a: 2.57, m	5a, 5b, 6b, 12a		5a, 6b, 19
			b: 2.36, m	5a, 5b, 6a	4, 7, 8, 12	5b, 6a, 12b
7		149.0, C				
8		55.1, CH	2.59, brd (4.3)	11a, 11b	4, 6, 7, 11, 12, 13	11a, 11b, 12a, 13, 19
9		86.5, C				
11		43.9, CH_2	a: 2.16, ddd (11.3, 4.3, 2.5)	5a, 8, 11b	9	8, 11b, 13
			b: 1.59, brd (11.3)	8, 11a, 19	7, 8, 9	8, 11a
12		110.7, CH_2	a: 4.75, t (2.4)	6a	6, 8	8
			b: 4.78, t (2.0)		6, 8	6b
13		138.9, CH	5.57, d (15.0)	14, 18	9, 15	8, 11a, 15, 19
14		126.2, CH	6.49, dd (15.0, 10.9)	13, 15	9, 13, 15, 16	17, 19
15		125.9, CH	5.81, dqq (10.9, 1.4, 0.8)	14, 17, 18	17, 18	13, 18
16		135.5, C				
17		18.8, CH_3	1.79, brs	15	15, 16, 18	14
18		26.2, CH_3	1.77, brs	13, 15	15, 16, 17	15
19		23.1, CH_3	1.26, s	11b	8, 9, 13	6a, 8, 13, 14
1'	80.0, C	82.8, C				
2'	87.7, CH	86.2, CH	4.68, brs	4'a	1', 3', 16'	4'a, 15', 16'
3'	209.4, C	211.0, C				
4'	37.6, CH_2	36.6, CH_2	a: 2.74, brtd (13.5, 7.2)	2', 4'b, 5'a, 5'b	3', 5'	2', 4'b, 5'b
			b: 2.21, m	4'a, 5'a, 5'b	2', 3', 6'	4'a, 5'a
5'	31.4, CH_2	32.7, CH_2	a: 2.11, td (13.6, 5.1)	4'a, 4'b, 5'b	3', 4', 6'	4'b, 5'b, 14'b
			b: 2.04, ddd (13.6, 7.3, 3.3)	4'a, 4'b, 5'a	1', 3', 4', 6'	4'a, 5'a
6'	62.2, C	76.7, C				
7'	61.9, C	62.5, C				
8'	58.2, CH	58.2, CH	2.97, t (6.5)	9'a, 9'b, 15'	1', 7', 9', 10'	9'a, 9'b, 14'a, 14'b
9'	28.4, CH_2	28.3, CH_2	a: 2.39, m	8', 9'b, 10', 13'	7', 8', 10', 11'	8', 9'b, 10', 12', 15'
			b: 2.25, m	8', 9'a, 10', 13'	7', 10', 11'	8', 9'a, 10', 15'
10'	120.0, CH	119.7, CH	5.27, t hept (7.4, 1.4)	9'a, 9'b, 12', 13'	9', 12', 13'	9'a, 9'b, 13'
11'	136.4, C	136.2, C				
12'	18.4, CH_3	18.2, CH_3	1.68, brd (1.0)	10'	10', 11', 13'	9'a
13'	26.2, CH_3	26.1, CH_3	1.72, brq (1.1)	9'a, 9'b, 10'	10', 11', 12'	10'
14'	52.0, CH_2	70.1, CH_2	a: 4.26, brd (10.9)	14'b	1, 5', 6'	8', 15'
			b: 4.19, d (10.9)	14'a	1, 5'	5'a, 8'
15'	15.3, CH_3	16.3, CH_3	1.55, s	8'	1', 7', 8'	2', 9'a, 9'b, 14'a, 16'
16'	59.6, CH_3	59.7, CH_3	3.49, s		2'	2', 15'

Table S6. Key $\Delta\delta$ (= δ_S–δ_R) data table for the *S*- and *R*-MTPA Mosher esters of pseudallicin B (**4**)

			$\Delta\delta$ (=δ_S – δ_R)	
Position	δ_H ***S*-ester (2S) (ppm)**	δ_H ***R*-ester (2R) (ppm)**	ppm	HZ (600 MHz)
3	a: 2.42	a: 2.35	+0.07	+42
	b: 2.24	b: 2.11	+0.13	+78

Table S7. Full NMR data table for pseudallicin C (**5**) and comparison with the ^{13}C spectrum of tyroscherin formate

	Literature[4]	**Experimental**				
position	**Tyoscherine Formate δ_C, type**	**δ_C, type**	**δ_H (*J* in Hz)**	**COSY**	**HMBC**	**NOESY**
2		170.2, C				
3		138.8, C				
4		121.1, CH	5.49, s	MeN	2, 5	6a, 10a, MeN
5		84.4, C				
6		38.9, CH_2	a: 1.70, dd (14.5, 5.5)	6b, 7		4
			b: 1.65, ddd (14.5, 4.1, 1.9)	6a, 7, 10b		7, 19
7		45.2, CH	2.52, brdt (10.6, 4.7)	6a, 6b, 11, 18b		6b, 18b, 19
8		n.d.				
9		30.1, CH_2	a: 2.45, brtd (12.9, 4.5)	9b, 10a, 10b, 18a		9b, 10b
			b: 2.11, brdt (13.8, 4.5)	9a, 10a, 10b, 18a		9a
10		38.9, CH_2	a: 1.45, ddd (13.3, 11.9, 4.7)	9a, 9b, 10b		4, 10b, 11
			b: 1.29, m	6b, 9a, 9b, 10a	5	9a, 10b
11		47.7, CH	3.23, dq (10.6, 6.8)	7, 19		9a, 19
12		215.5, C				
13		43.5, CH_2	3.07-3.14, m	14, 17		
14		116.7, CH	5.21, tsept (7.2, 1.4)	13, 16, 17		17
15		136.7, C				
16		18.0, CH_3	1.61, brs	14, 17	14, 15, 17	
17		25.8, CH_3	1.73, brs	13, 14, 16	14, 15, 16	14
18		111.0, CH_2	a: 4.72, brt (1.5)	9a, 9b	7	9b, 18b
			b: 4.55, brd (2.0)	7	7, 9	7, 18a
19		15.3, CH_3	0.96, d (6.8)	11	7, 11, 12	6b, 7, 11
1'	32.4, CH_2	34.8, CH_2	a: 3.09, dd (13.1, 3.4)	1'b, 2', 3"/5"	1"	1'b, 2', 2"/6"
			b: 2.65, dd (13.1, 11.7)	1'a, 2'	3', 1"	1'a, 2"/6"
2'	66.6, CH	62.5, CH	4.76, ddd (11.7, 8.2, 3.4)	1'a, 1'b, 3'		1'a, 3', 2"/6"
3'	68.7, CH	73.2, CH	3.68, brtd (8.5, 3.1)	2', 4'a, 4'b		2', 4'a, MeN
4'	33.0, CH_2	35.9, CH_2	a: 1.66, m	3', 4'b, 5'a, 5'b		3', 4'b
			b: 1.49, dtd (14.1, 9.1, 5.1)	3', 4'a, 5'a, 5'b		4'a
5'	29.8, CH_2	29.5, CH_2	a: 2.24, m	4'a, 4'b, 5'b, 6'		5'b
			b: 2.09, m	4'a, 4'b, 5'a, 6'		5'a
6'	128.3, CH	129.4, CH	5.41, brdt (15.3, 6.8)	5'a, 5'b, 7'		8'
7'	138.6, CH	137.7, CH	5.24, ddt (15.3, 8.3, 1.2)	6', 8'		8', 9'a, 13'
8'	35.6, CH	35.8, CH	2.16, m	5', 9', 13'		6', 7', 13', 14'
9'	45.5, CH_2	45.6, CH_2	a: 1.24, ddd (13.3, 9.9, 4.6)	8', 9'b	8', 10'	7', 9'b, 13'
			b: 1.00, ddd (13.3, 9.2, 5.0)	8', 9'a, 10'		9'a, 10'
10'	33.0, CH	33.0, CH	1.35, m	9'b, 14'		9'b, 14'
11'	31.1, CH_2	31.2, CH_2	a: 1.28, m	11'b, 12'		12'
			b: 1.14, dquint (13.3, 7.4)	11'a, 12'		12'
12'	11.6, CH_3	11.5, CH_3	0.85, t (7.4)	11'a, 11'b	10', 11'	11'a, 11'b
13'	22.1, CH_3	22.4, CH_3	0.94, d (6.7)	8'	7', 8', 9'	7', 8', 9'a
14'	19.4, CH_3	19.2, CH_3	0.83, d (6.5)	10'	9', 10', 11'	8', 10'
1"	127.7, C	131.4, C				
2"/6"	131.1, CH	131.2, CH	6.98, brd (8.5)	3"/5"	1', 2"/6", 4"	1'a, 1'b, 2', 3"/5", MeN
3"/5"	116.7, CH	115.8, CH	6.61, brd (8.5)	1'a, 2"/6"	1", 3"/5", 4"	2"/6"
4"	157.9, C	156.4, C				
MeN	32.3, CH_3	33.0, CH_3	2.62, s	4	3, 2'	4, 3', 2"/6"

Table S8. Full NMR data table for pseudallicin D (**6**) and comparison with the ^{13}C spectrum of tyroscherin formate[2]

	Literature[4]	Experimental				
position	**Tyoscherine Formate δ_C, type**	**δ_C, type**	**δ_H (*J* in Hz)**	**COSY**	**HMBC**	**NOESY**
2		170.0, C				
3		138.7, C				
4		121.8, CH	5.33, s	MeN	2, 3, 5, 10	6a, 10a, MeN
5		84.2, C				
6		40.4, CH_2	1.72, dd (14.9, 5.9)	6b, 7	7	4, 6b, 7, 10a
			1.29, m	6a	7	6a, 7, 11
7		45.9, CH	2.50, brdd (11.4, 5.6)	6a, 11	8	6a, 6b, 18b, 19
8		147.8, C				
9		29.0, CH_2	a: 2.26, brtd (13.5, 4.3)	9b, 10a, 10b, 18a	8	9b, 10b, 11
			b: 2.10, m	9a, 10a		9b, 10a, 10b, 18a
10		38.7, CH_2	a: 1.46, m	9a, 9b, 10b	9	4, 6a, 9b, 10b
			b: 1.21, m	9a, 10a	8	9a, 9b, 10a
11		46.5, CH	3.27, dq (11.3, 7.0)	7, 19	12, 19	6b, 9a, 19
12		216.3, C				
13		44.0, CH_2	a: 3.33, dd (18.7, 7.6)	14, 17	12, 14, 15	13b, 14, 16
			b: 3.24, dd (18.7, 7.3)	14, 17	12, 14, 15	13a, 14, 16
14		116.9, CH	5.26, tsept (7.8, 1.4)	13a, 13b, 16, 17		13a, 13b, 17
15		136.4, C				
16		18.1, CH_3	1.58, brd (0.8)	14	14, 15, 17	13a, 13b
17		25.8, CH_3	1.72, brq (1.2)	13a, 13b, 14	14, 15, 16	14
18		111.6, CH_2	a: 4.83, brt (2.0)	9a	7, 9	9b
			b: 4.74, brd (2.4)		7, 9	7, 19
19		17.3, CH_3	0.90, d (7.0)	11	7, 11, 12	7, 11, 18b
1'	32.4, CH_2	34.7, CH_2	a: 3.09, dd (14.2, 3.4)	1'b, 2'	1"	1'b, 2', 2"/6"
			b: 2.63, dd (14.2, 11.6)	1'a, 2'	2', 1"	1'a, 2', 3', 2"/6"
2'	66.6, CH	62.4, CH	4.77, ddd (11.7, 8.4, 3.6)	1'a, 1'b, 3'		1'a, 1'b, 4'b, 2"/6"
3'	68.7, CH	73.1, CH	3.66, brtd (8.4, 3.0)	2', 4'a, 4'b		1'b, 4'a, 4'b, 5'b, MeN
4'	33.0, CH_2	35.8, CH_2	a: 1.65, m	3', 4'b, 5'a		3', 4'b
			b: 1.47, dtd (14.1, 9.2, 5.1)	3', 4'a, 5'a, 5'b		2', 3', 4'b
5'	29.8, CH_2	29.5, CH_2	a: 2.24, m	4'a, 4'b, 5'b, 6'		6'
			b: 2.09, m	4'a, 5'a, 6'	6', 7'	3', 6', 7'
6'	128.3, CH	129.3, CH	5.39, brdt (15.2, 6.8)	5'a, 5'b, 7'	5', 7', 8'	5'a, 5'b, 8', 13'
7'	138.6, CH	137.7, CH	5.24, ddt (15.2, 8.3, 1.2)	6', 8'	5', 6'	5'b, 9'b, 13'
8'	35.6, CH	35.6, CH	2.17, m	7', 9'a, 13'		6', 9'b, 13', 14'
9'	45.5, CH_2	45.4, CH_2	a: 1.25, ddd (13.4, 9.5, 4.3)	8', 9'b	7', 8', 10', 11', 13'	9'b, 13'
			b: 1.00, ddd (13.4, 9.0, 5.0)	9'a, 10'	7', 8', 10', 11', 13'	7', 8', 9'a, 14'
10'	33.0, CH	33.0, CH	1.35, m	9'b, 14'		9'b, 11'b, 14'
11'	31.1, CH_2	31.0, CH_2	a: 1.28, m	11'b, 12'	10'	11'b, 12', 14'
			b: 1.14, dquint (13.4, 7.2)	11'a, 12'	10'	10', 11'a, 12', 14'
12'	11.6, CH_3	11.5, CH_3	0.85, t (7.5)	11'a, 11'b	10', 11'	11'a, 11'b
13'	22.1, CH_3	22.3, CH_3	0.95, d (6.7)	8'	7', 8', 9'	6', 7', 8', 9'a
14'	19.4, CH_3	19.2, CH_3	0.84, d (6.6)	10'	9', 10', 11'	8', 9'b, 10', 11'a, 11'b
1"	127.7, C	131.4, C				
2"/6"	131.1, CH	131.1, CH	6.96, brd (8.5)	3"/5"	1', 2"/6", 4"	1'a, 1'b, 2', 3"/5"
3"/5"	116.7, CH	115.7, CH	6.60, brd (8.5)	2"/6"	1", 3"/5", 4"	2"/6"
4"	157.9, C	156.5, C				
MeN	32.3, CH_3	32.9, CH_3	2.58, s	4	3, 4, 2'	4, 3'

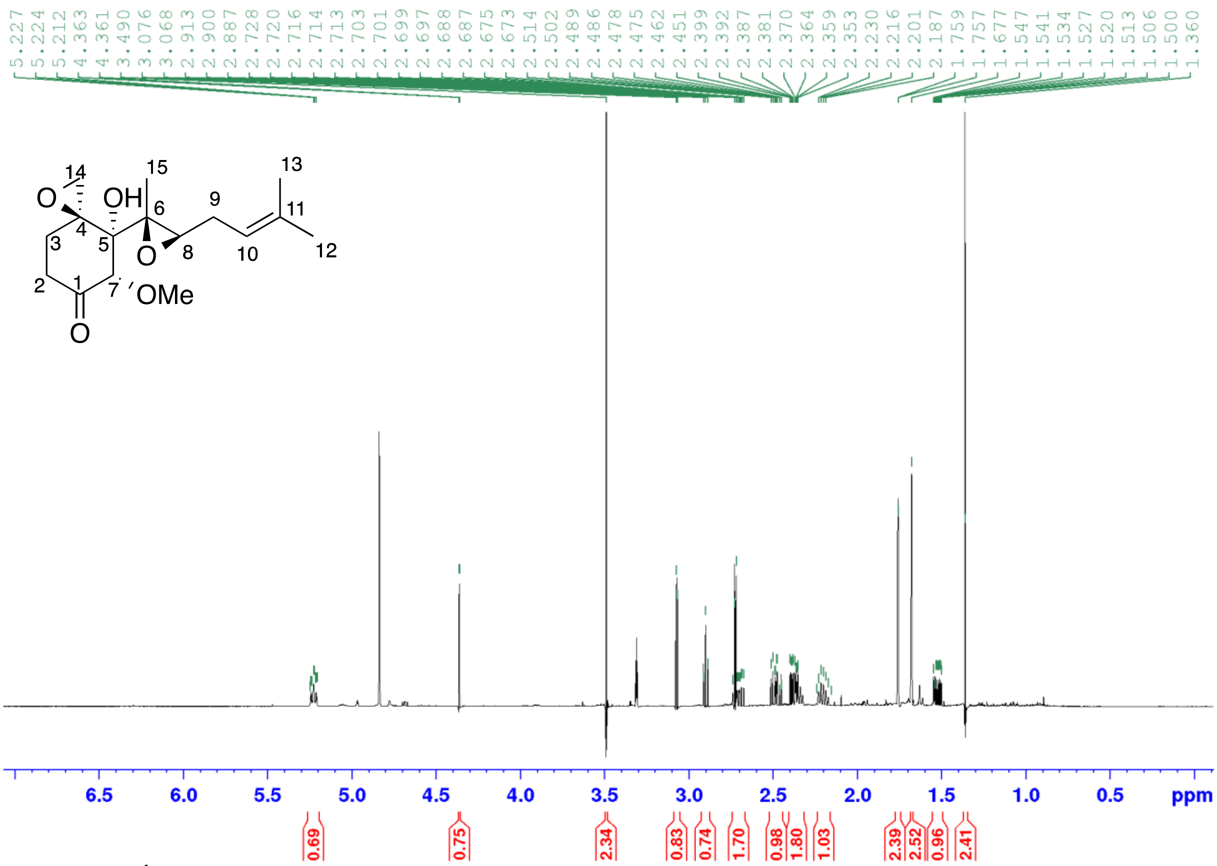


Figure S1. ^{1}H NMR (500 MHz, CD_3OD) spectrum of ovalicin (**1**)

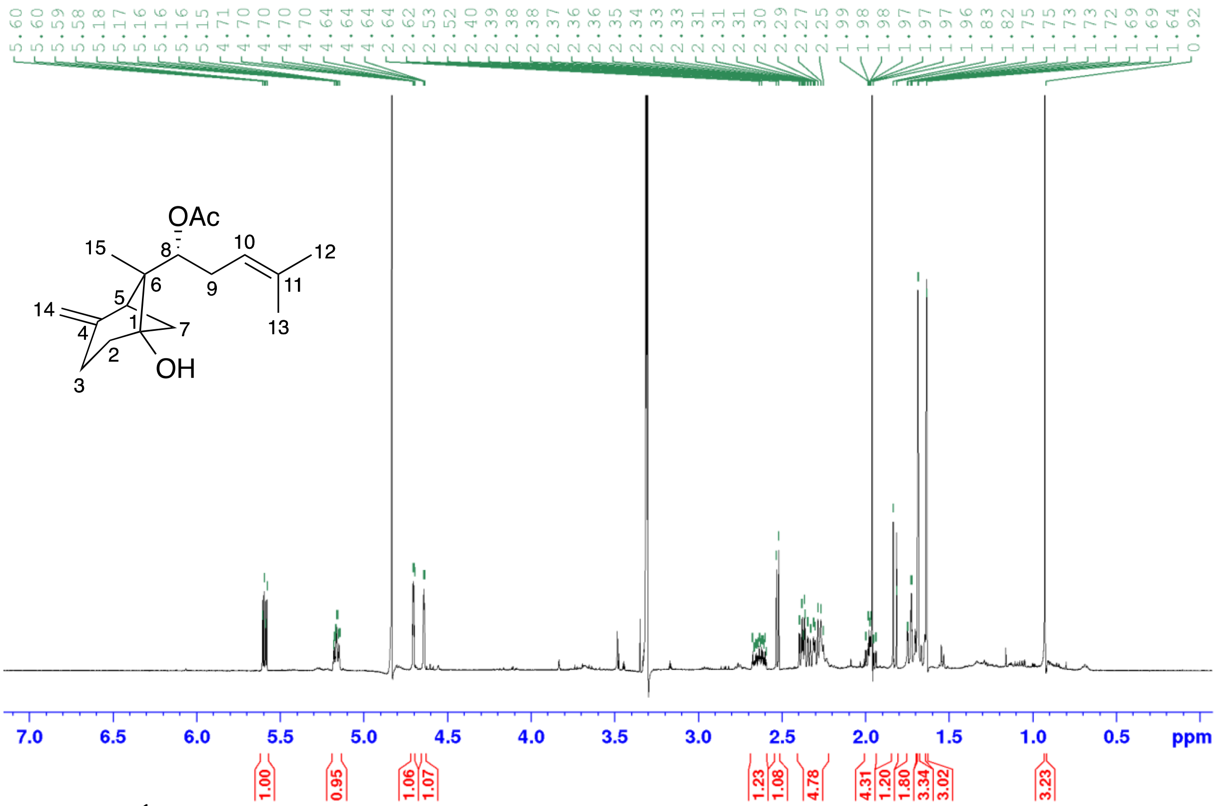


Figure S2. ^{1}H NMR (500 MHz, CD_3OD) spectrum of 5-hydroxy-8-acetoxy-*trans*-bergamotene (**2**)

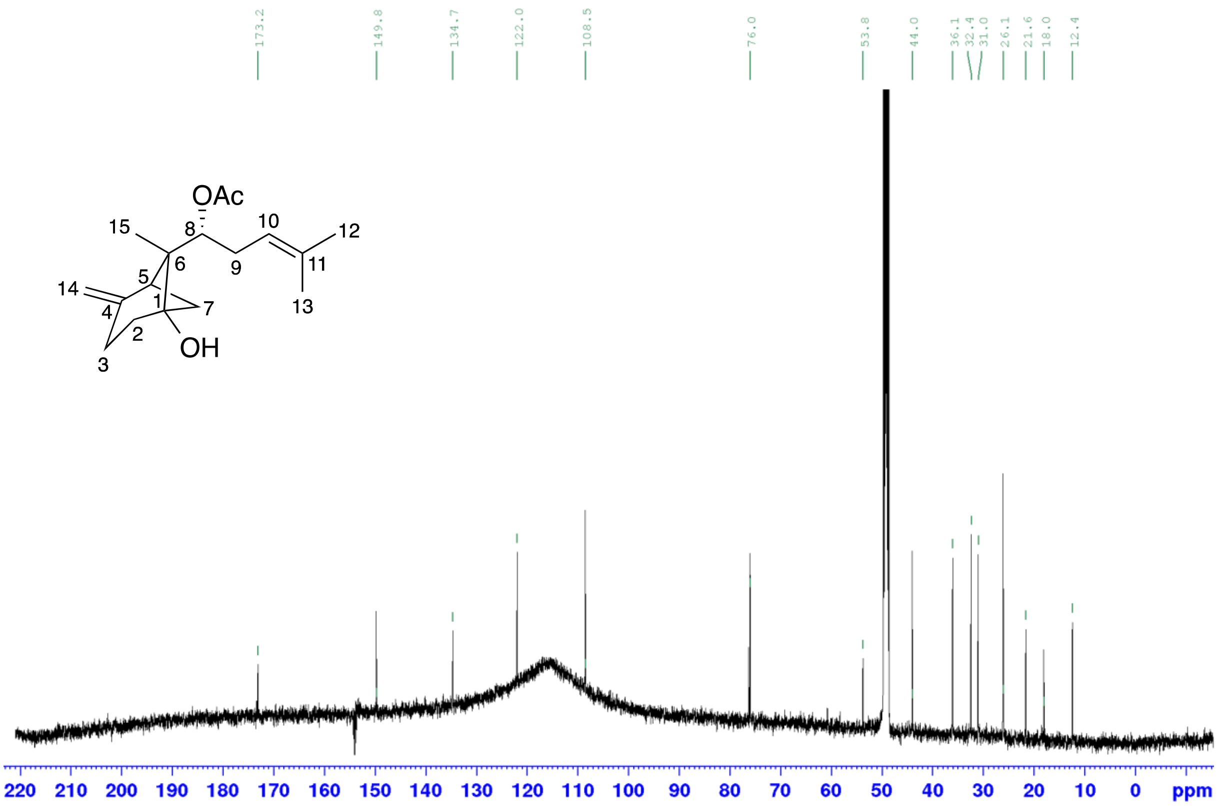


Figure S3. ^{13}C NMR (125 MHz, CD_3OD) spectrum of 5-hydroxy-8-acetoxy-*trans*-bergamotene (**2**)

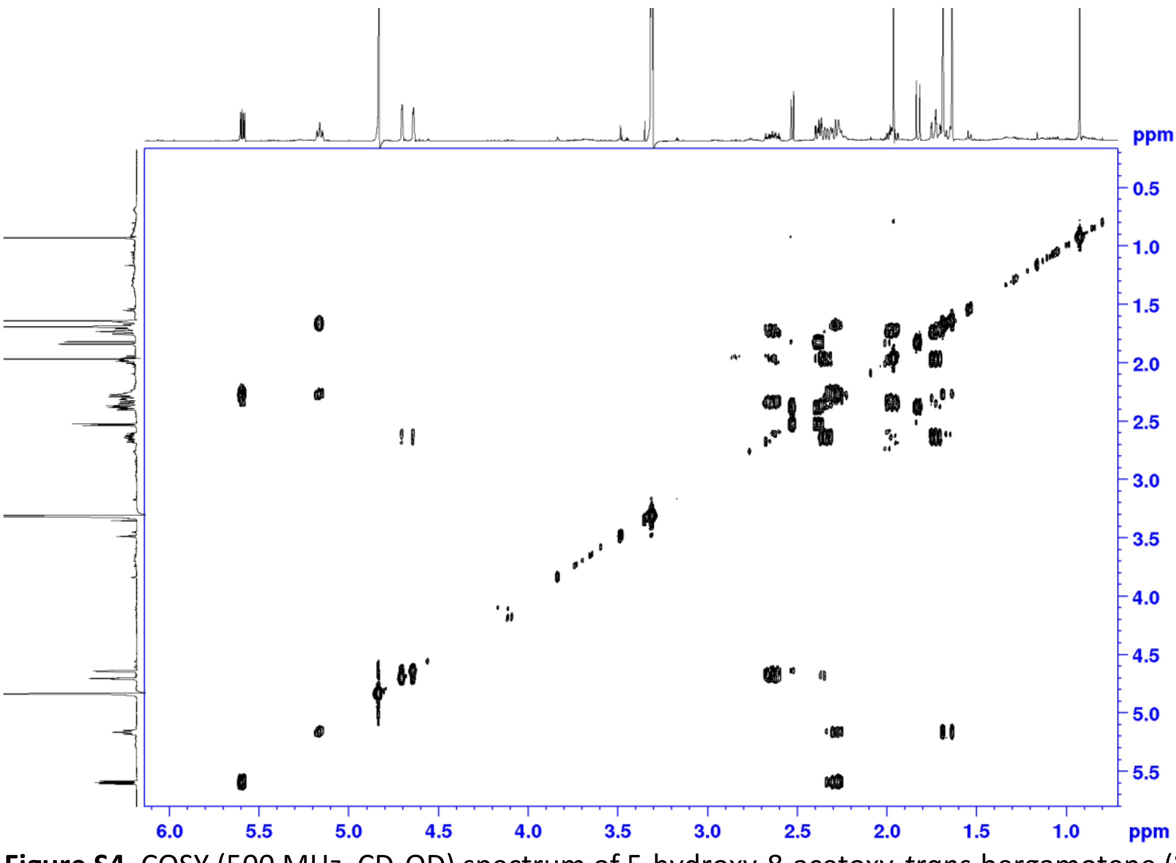


Figure S4. COSY (500 MHz, CD_3OD) spectrum of 5-hydroxy-8-acetoxy-*trans*-bergamotene (**2**)

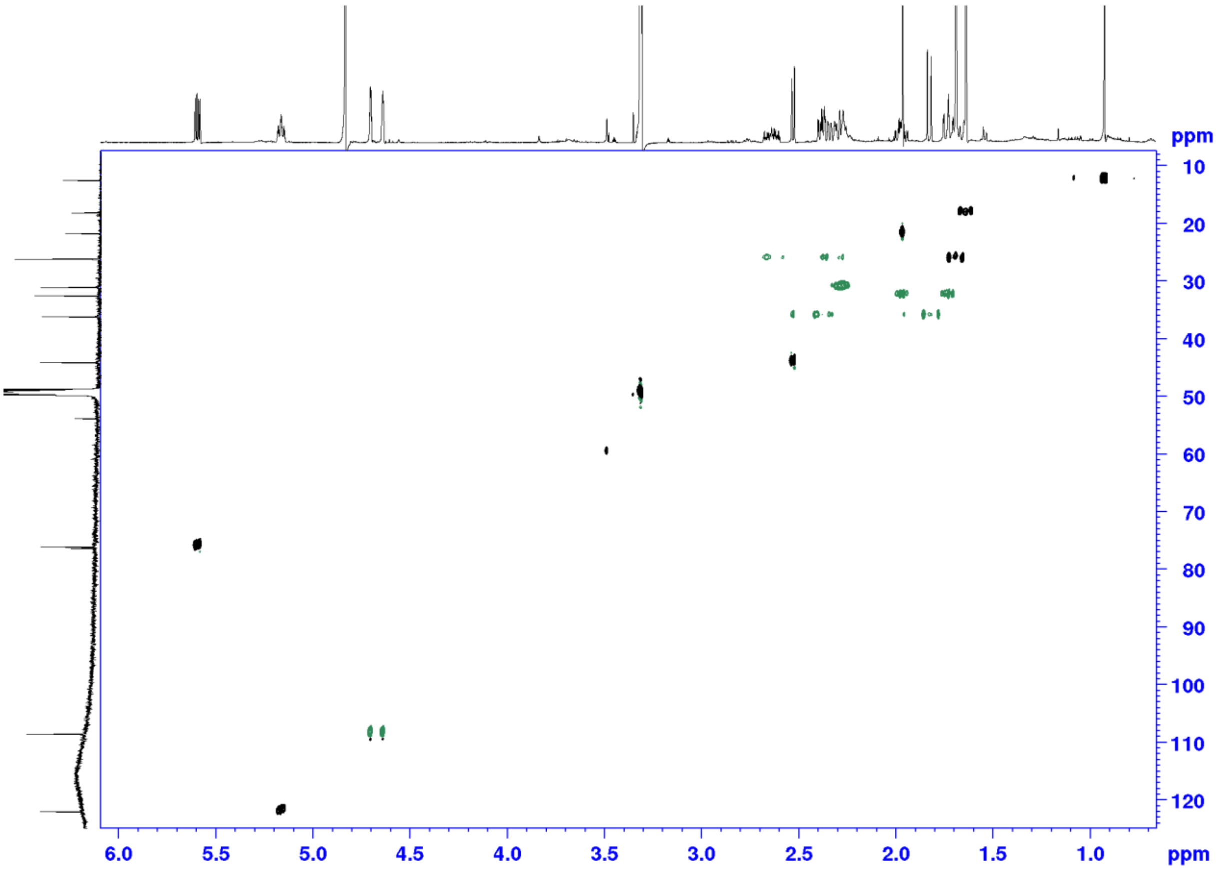


Figure S5. HSQC spectrum of 5-hydroxy-8-acetoxy-*trans*-bergamotene (**2**) in CD_3OD

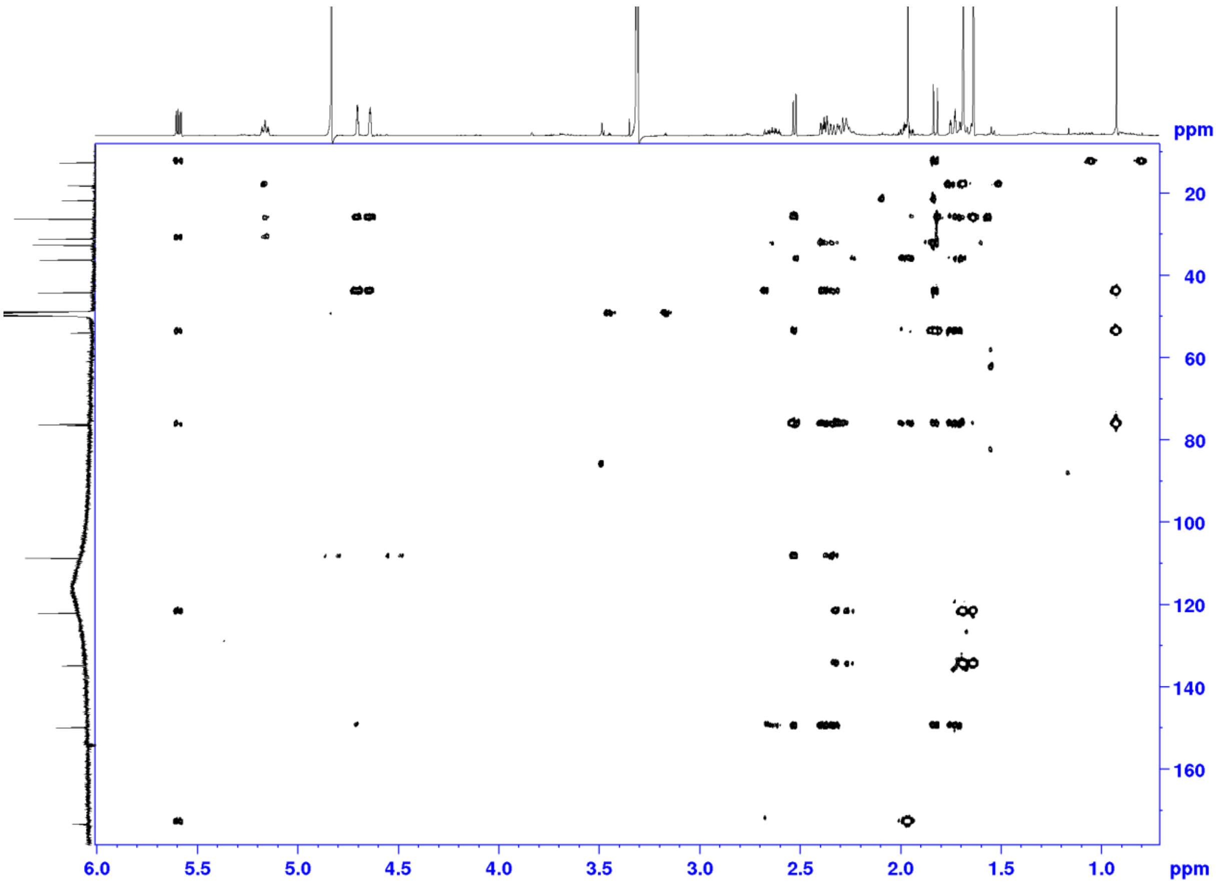


Figure S6. HMBC spectrum of 5-hydroxy-8-acetoxy-*trans*-bergamotene (**2**) in CD_3OD

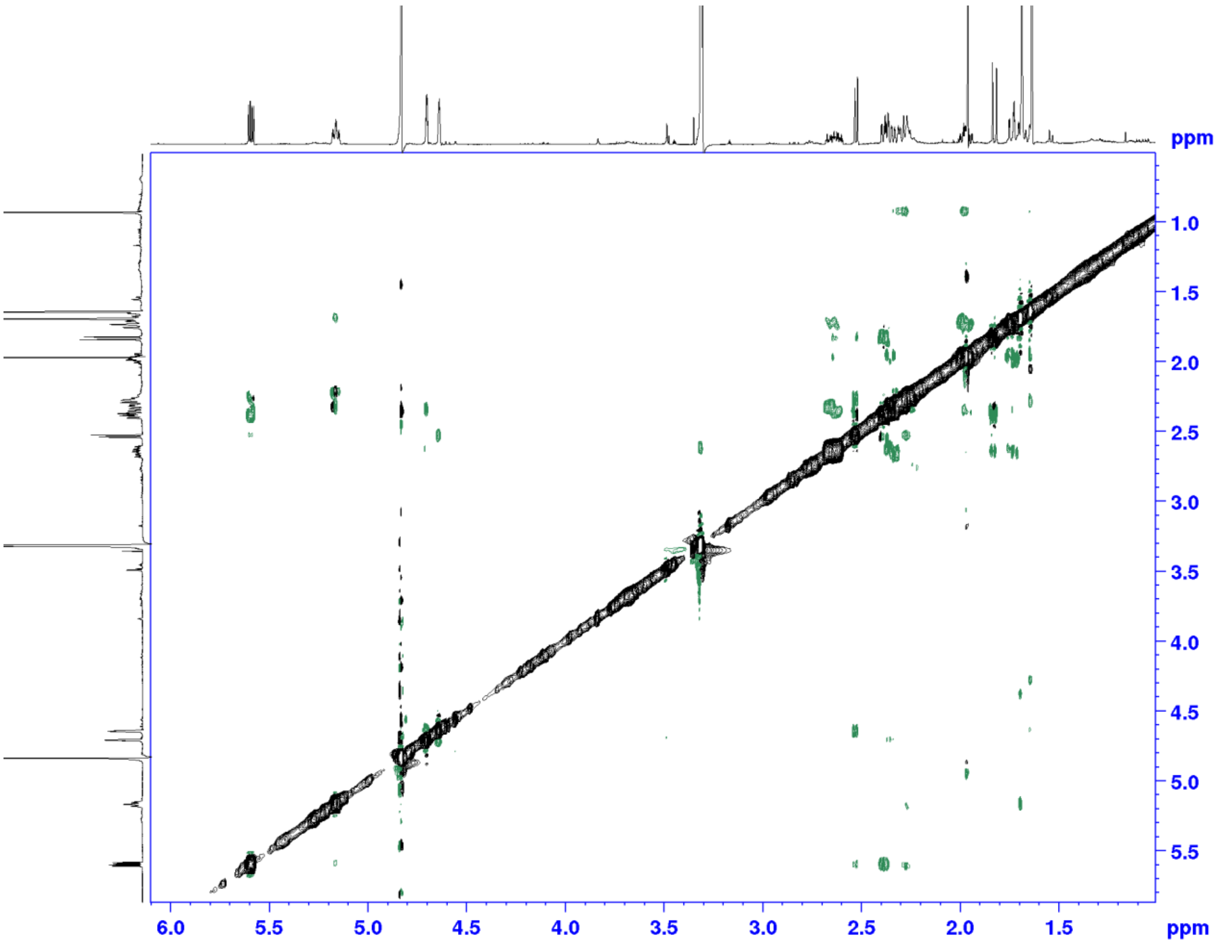


Figure S7. NOESY (500 MHz, CD_3OD) spectrum of 5-hydroxy-8-acetoxy-*trans*-bergamotene (**2**)

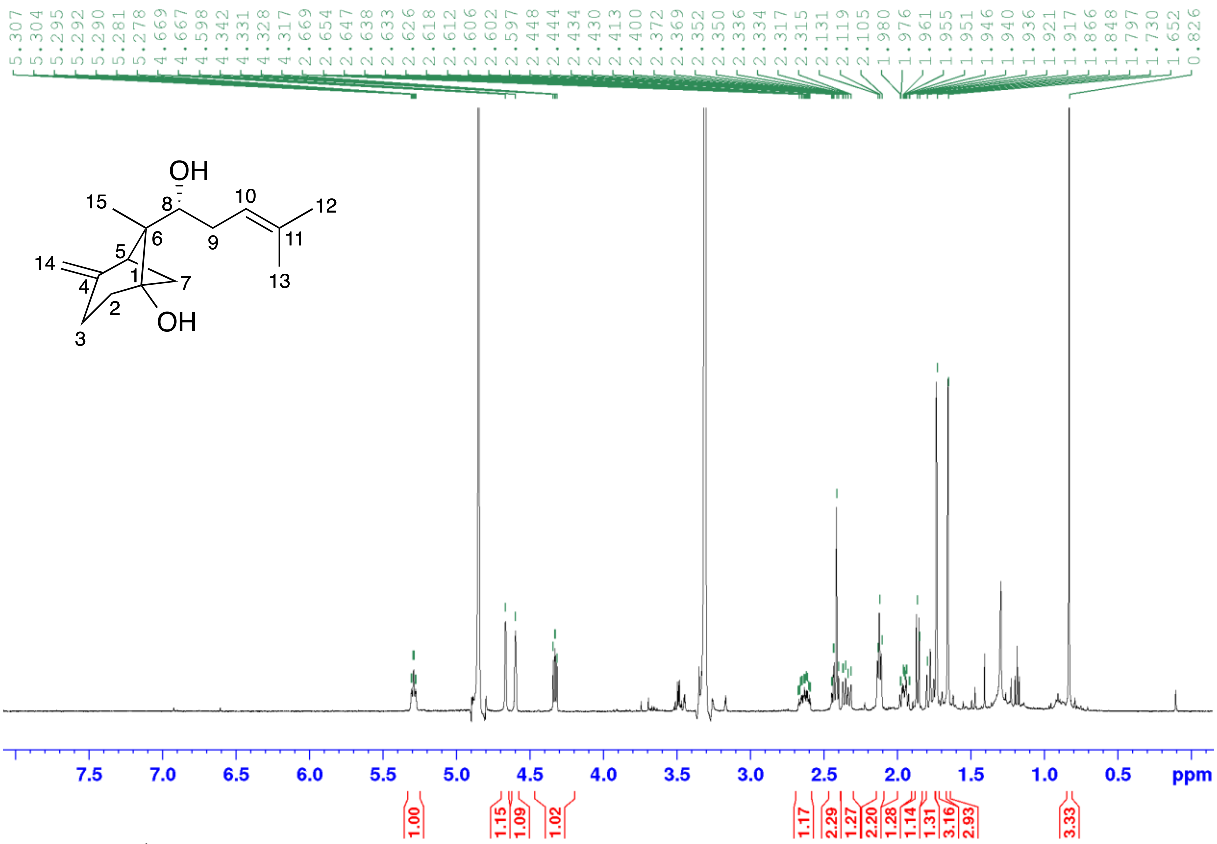


Figure S8. ^{1}H (500 MHz, CD_3OD) spectrum of 5,8-dihydroxy-*trans*-bergamotene

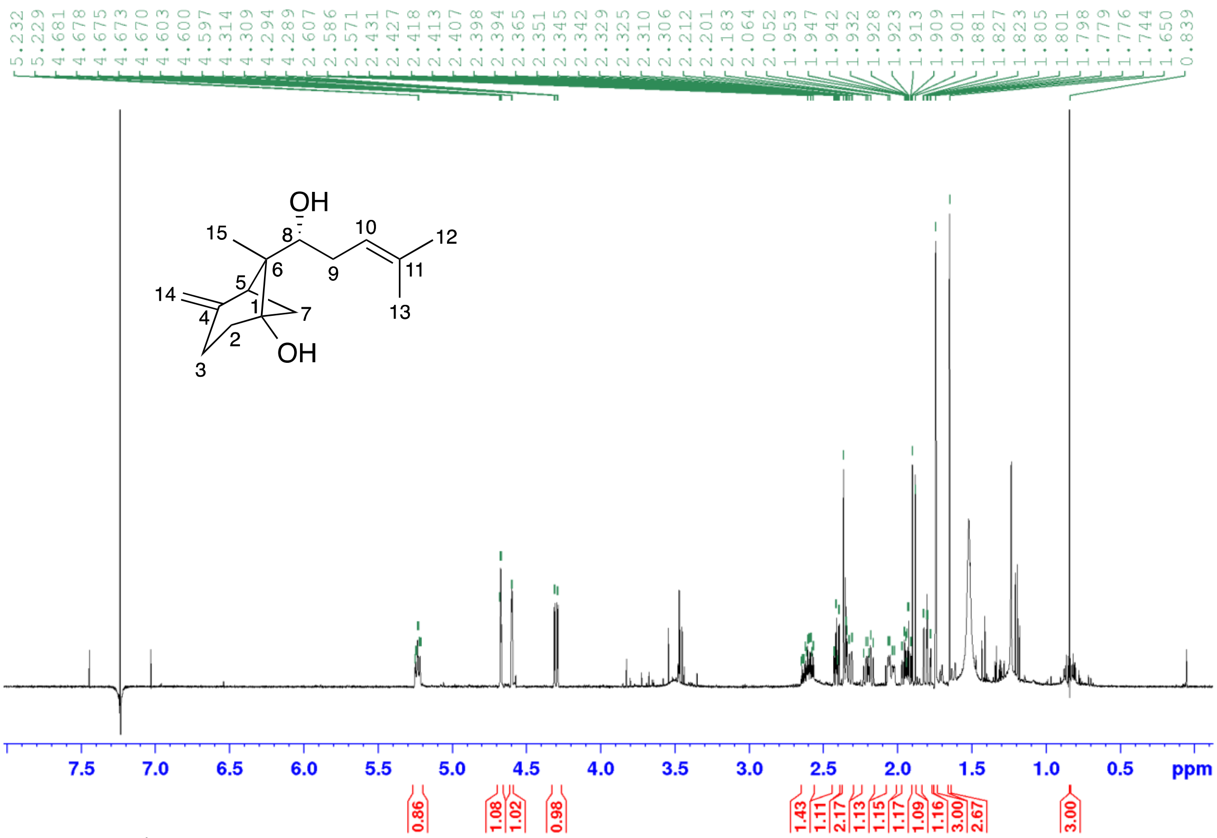


Figure S9. ^{1}H (500 MHz, $CDCl_3$) spectrum of 5,8-dihydroxy-*trans*-bergamotene

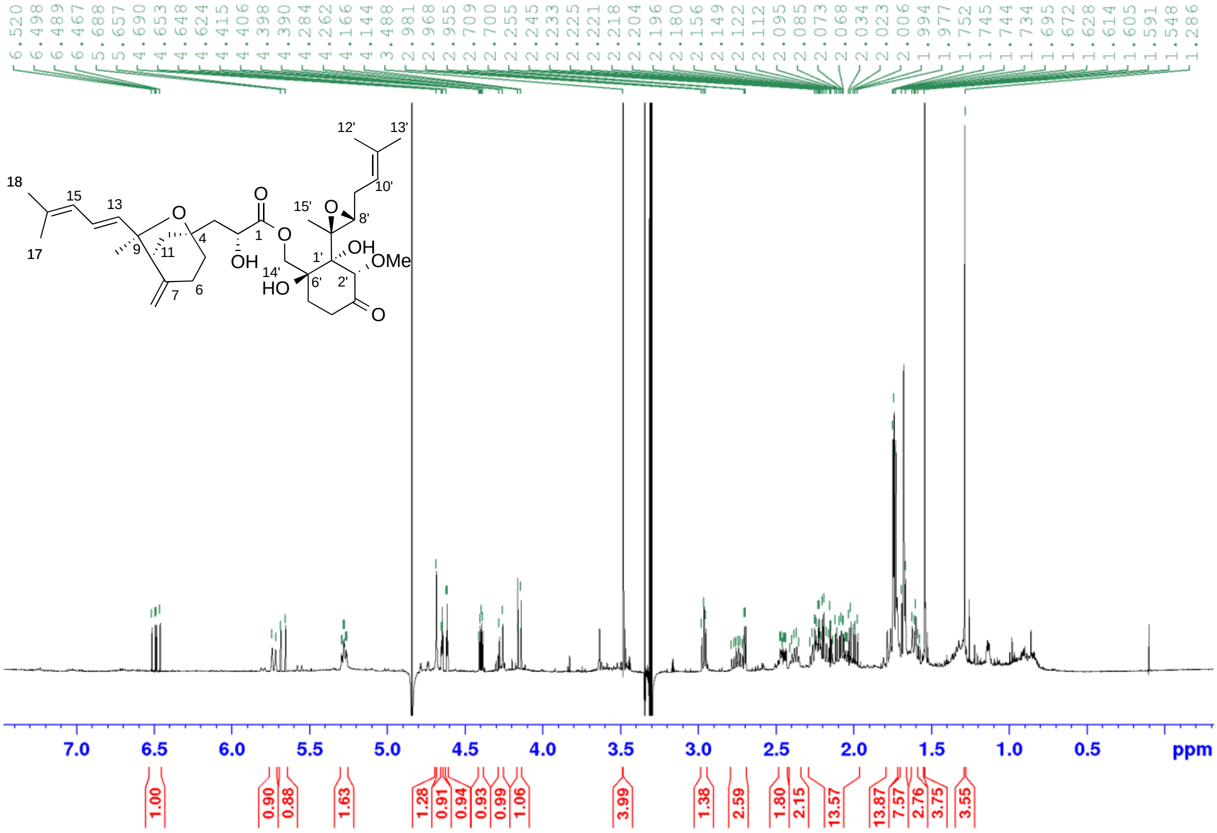


Figure S10. ^{1}H (500 MHz, CD_3OD) spectrum of pseudallicin A (**3**)

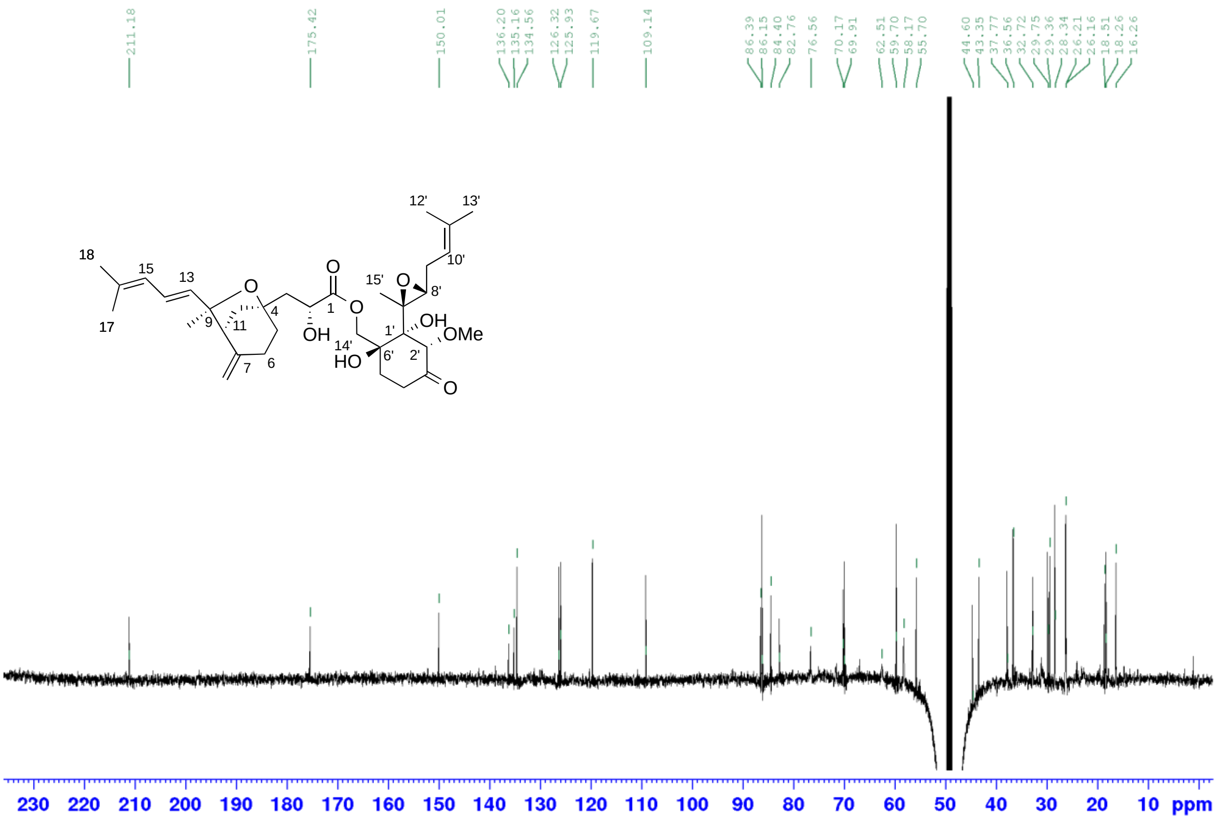


Figure S11. ^{13}C (150 MHz, CD_3OD) spectrum of pseudallicin A (**3**)

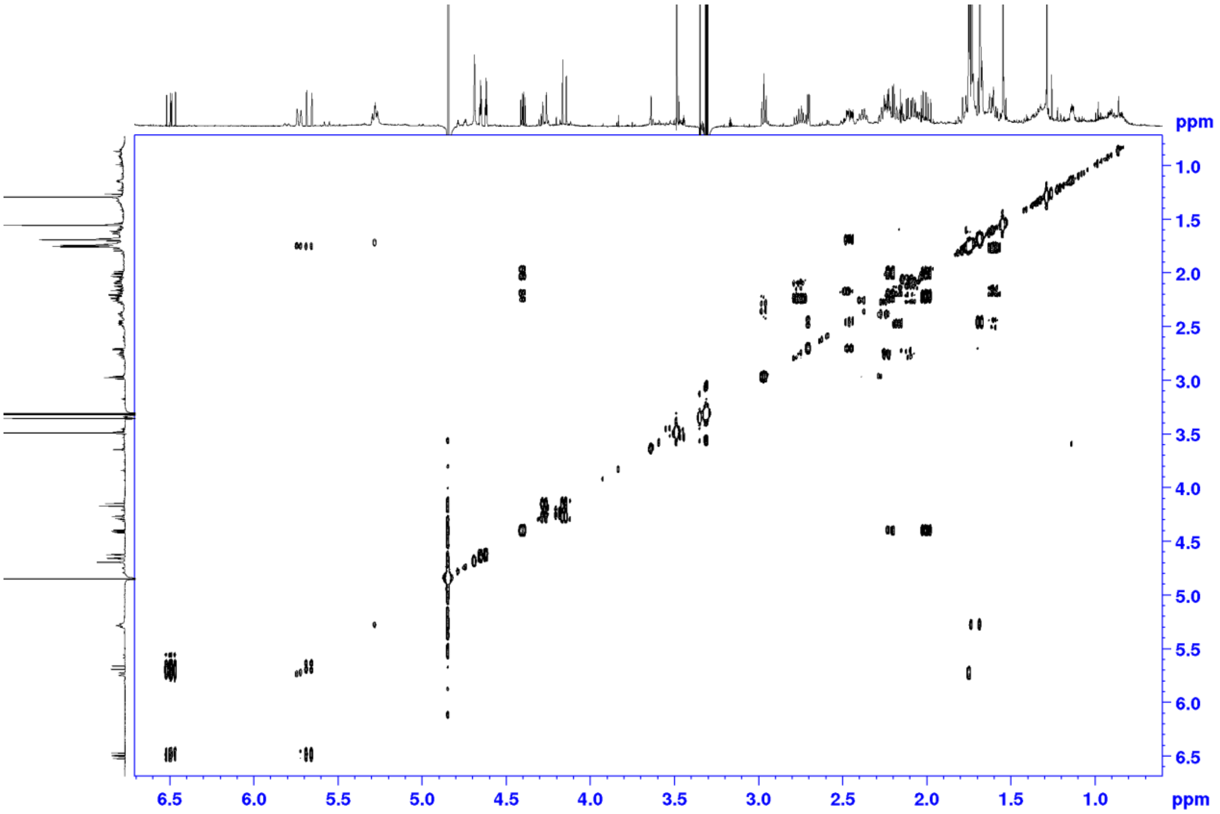


Figure S12. COSY (500 MHz, CD_3OD) spectrum of pseudallicin A (**3**)

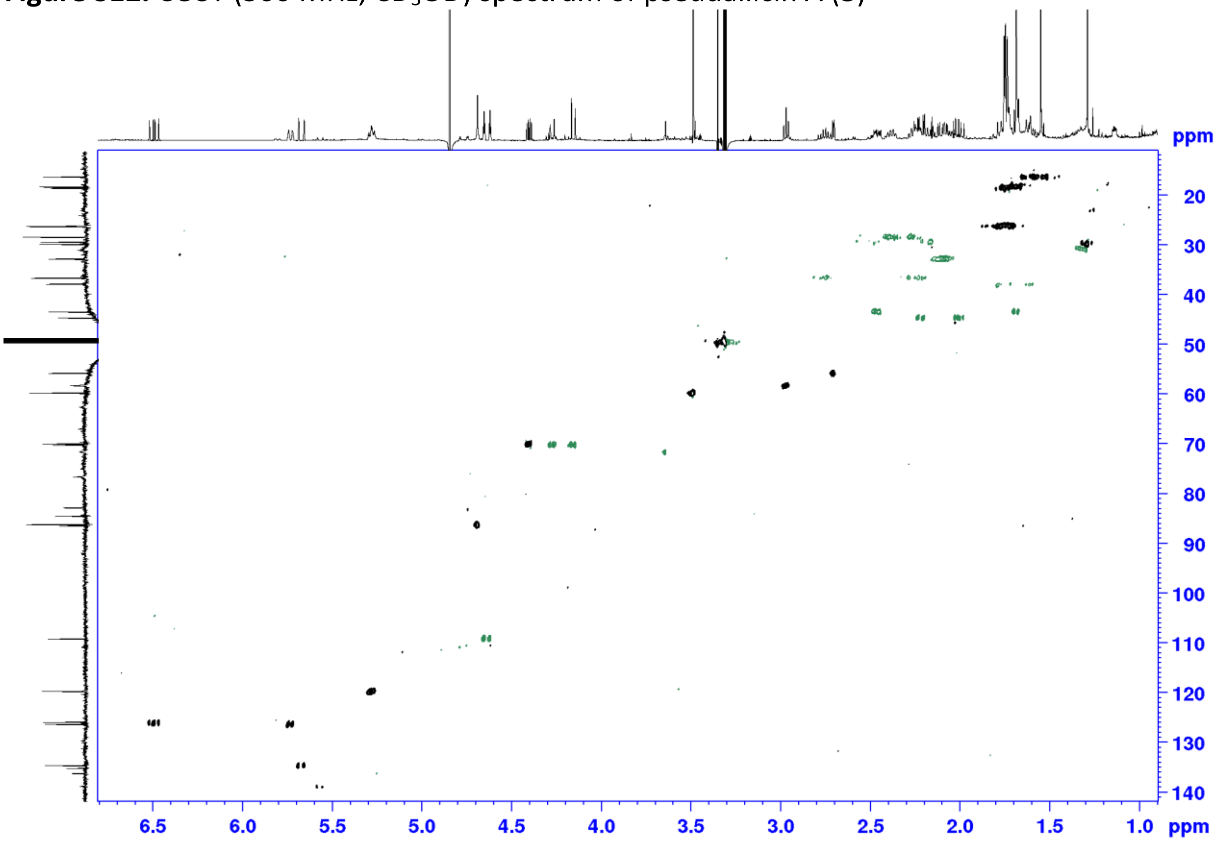


Figure S13. HSQC spectrum of pseudallicin A (**3**) in CD_3OD

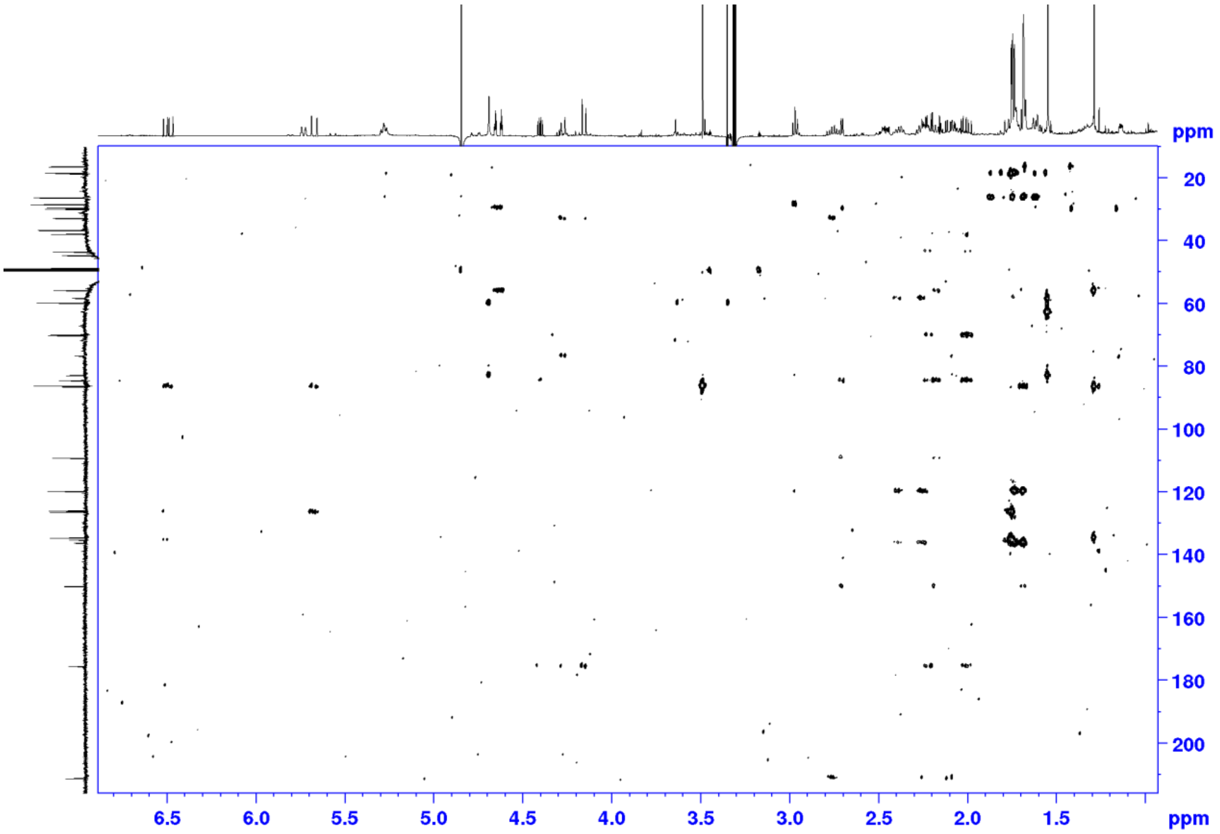


Figure S14. HMBC spectrum of pseudallicin A (**3**) in CD_3OD

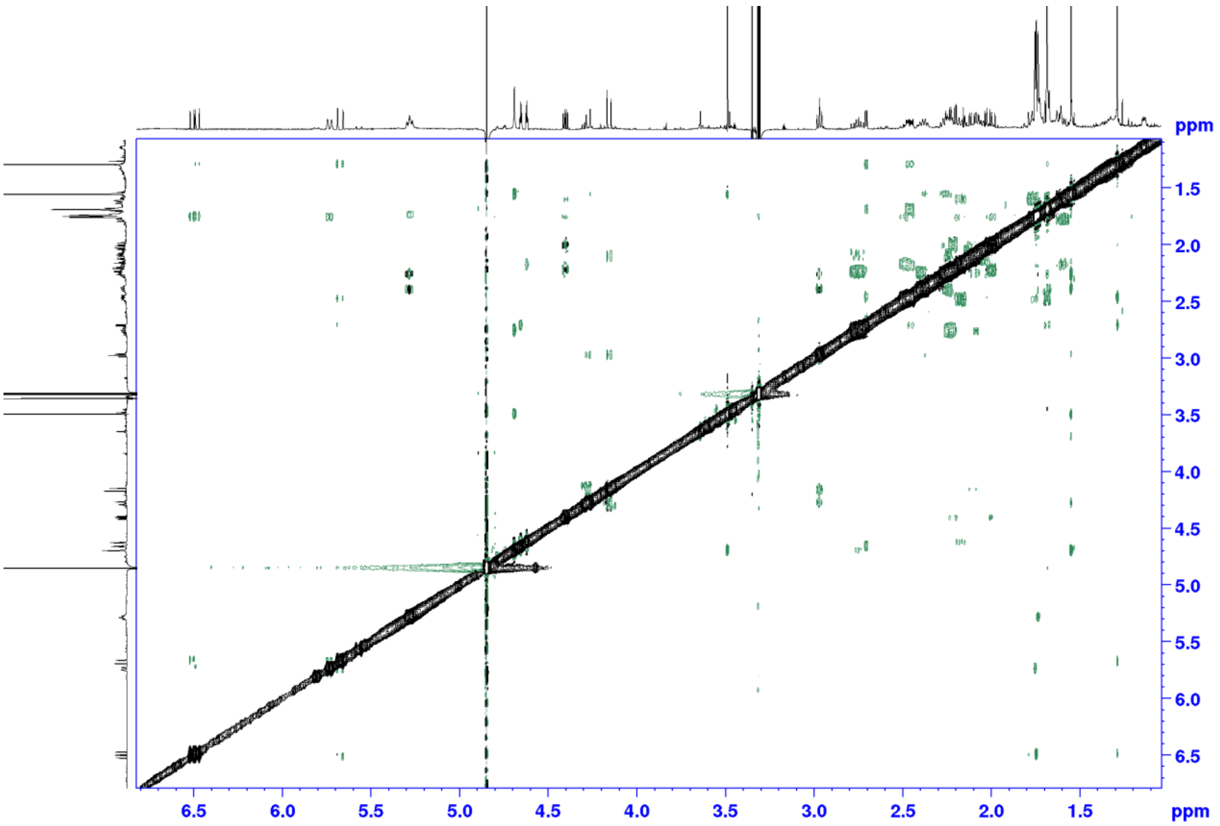


Figure S15. NOESY (500 MHz, CD_3OD) spectrum of pseudallicin A (**3**)

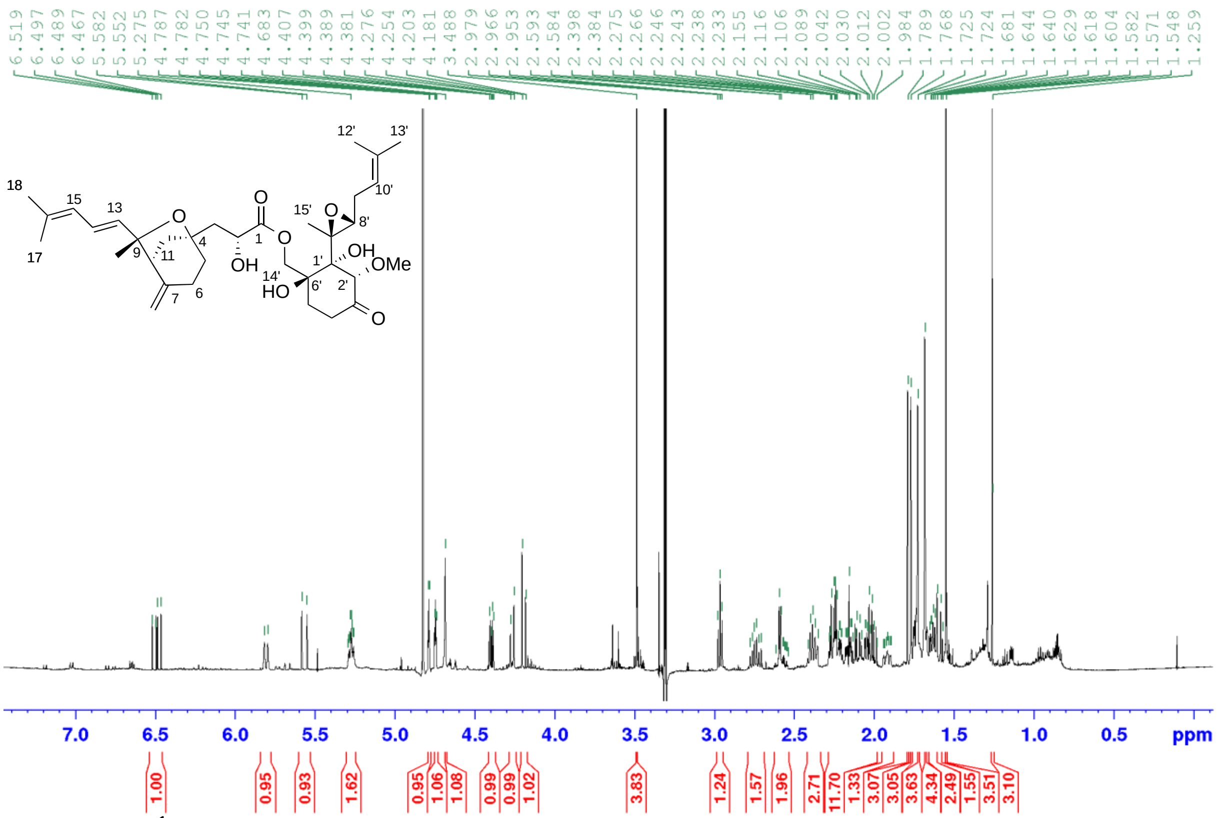


Figure S16. ^{1}H (500 MHz, CD_3OD) spectrum of pseudallicin B (**4**)

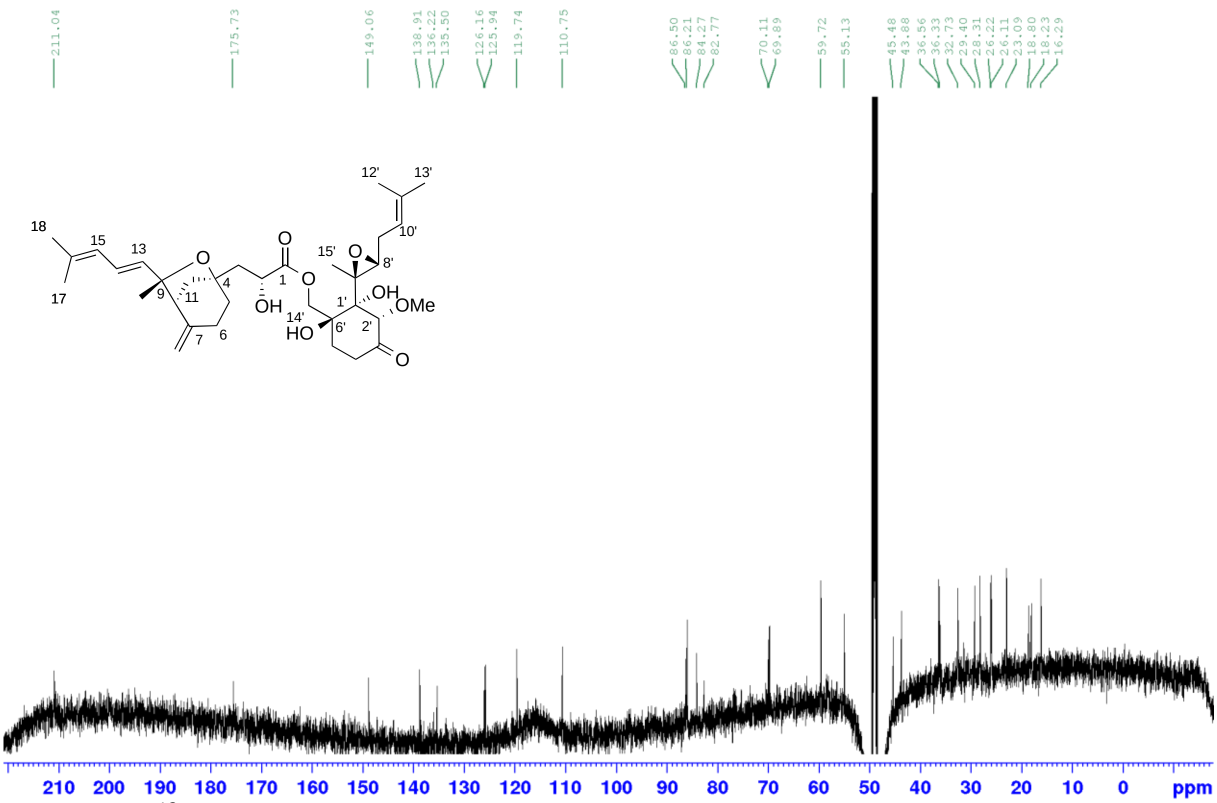


Figure S17. ^{13}C (125 MHz, CD_3OD) spectrum of pseudallicin B (**4**)

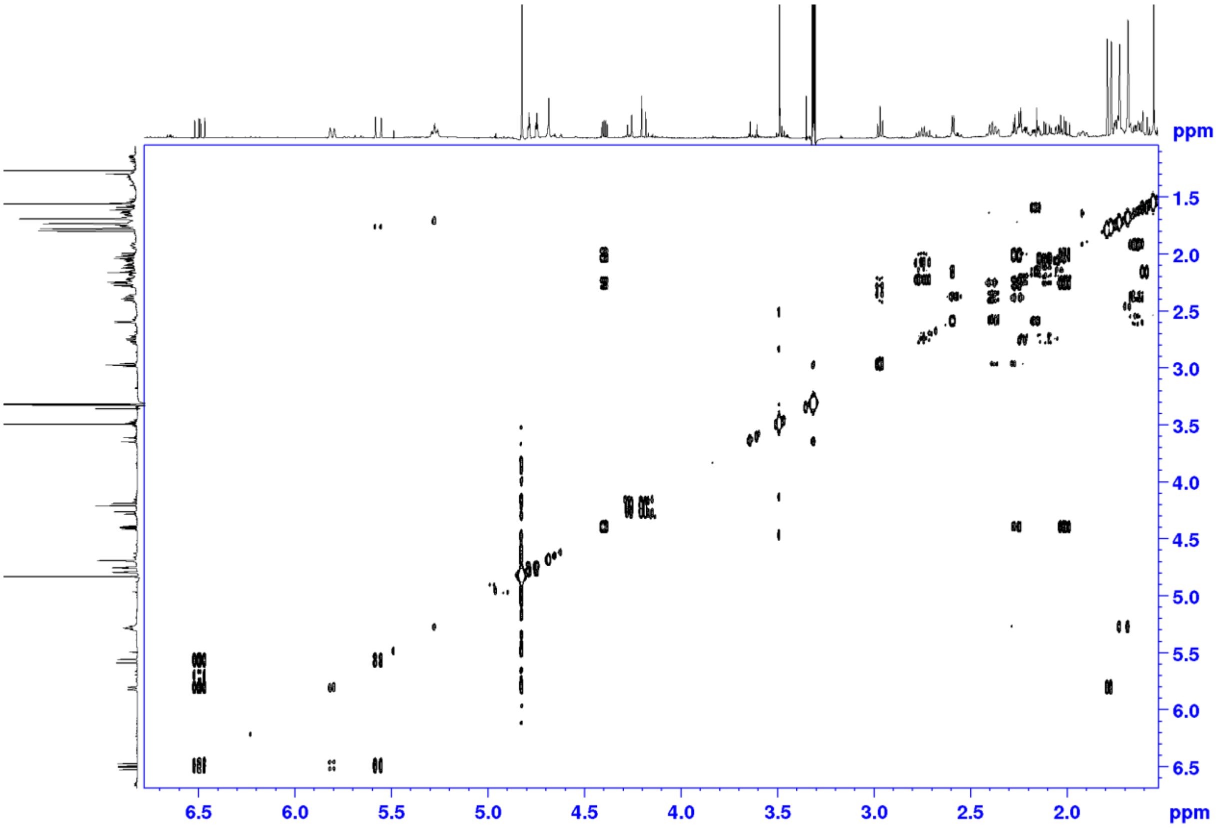


Figure S18. COSY (500 MHz, CD_3OD) spectrum of pseudallicin B (**4**)

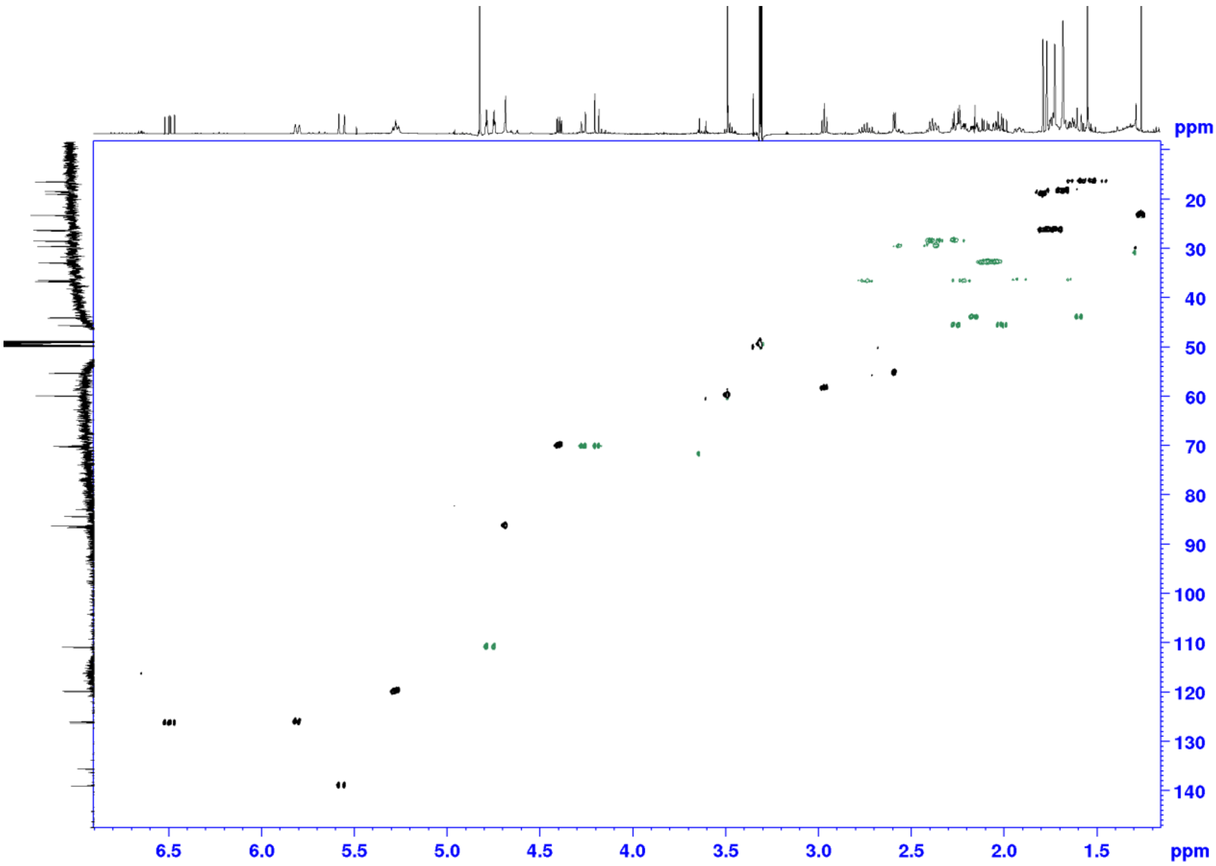


Figure S19. HSQC spectrum of pseudallicin B (**4**) in CD_3OD

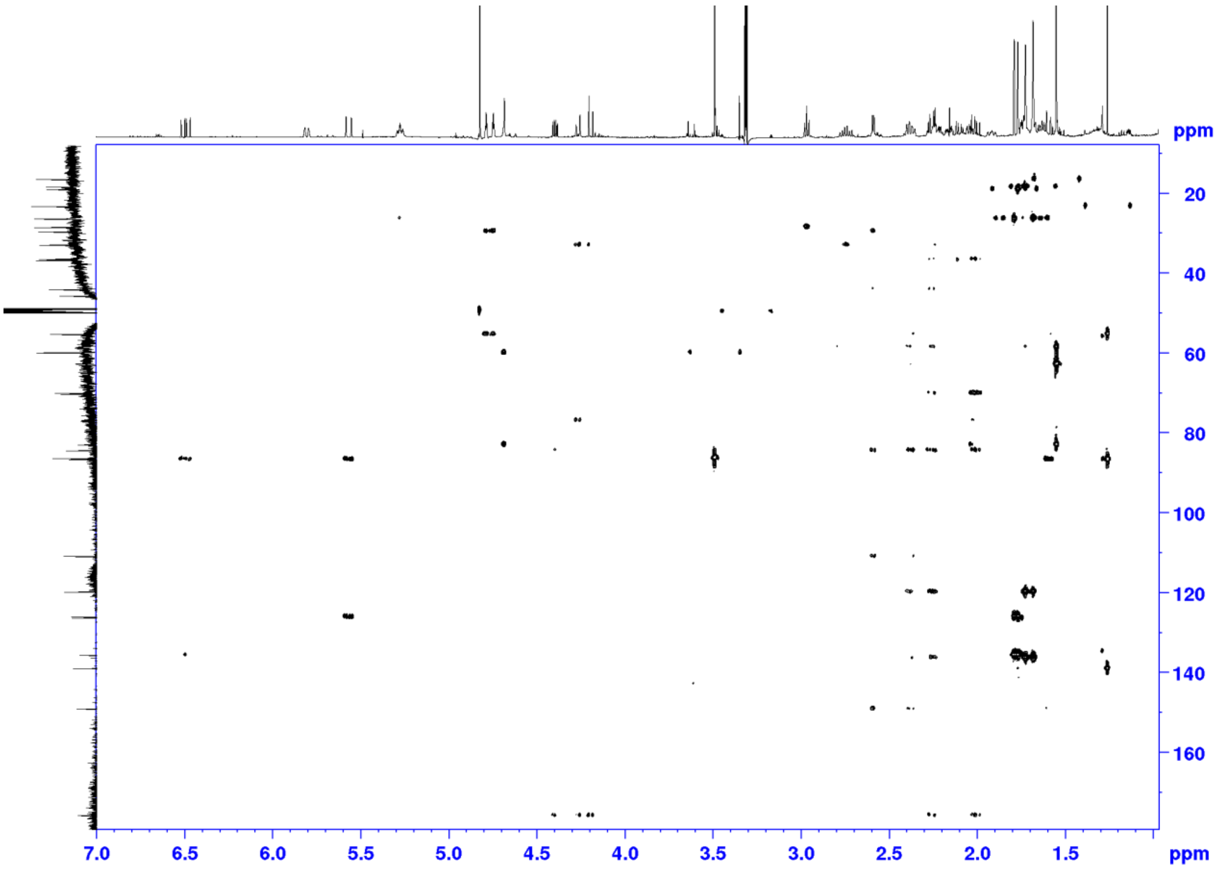


Figure S20. HMBC spectrum of pseudallicin B (**4**) in CD_3OD

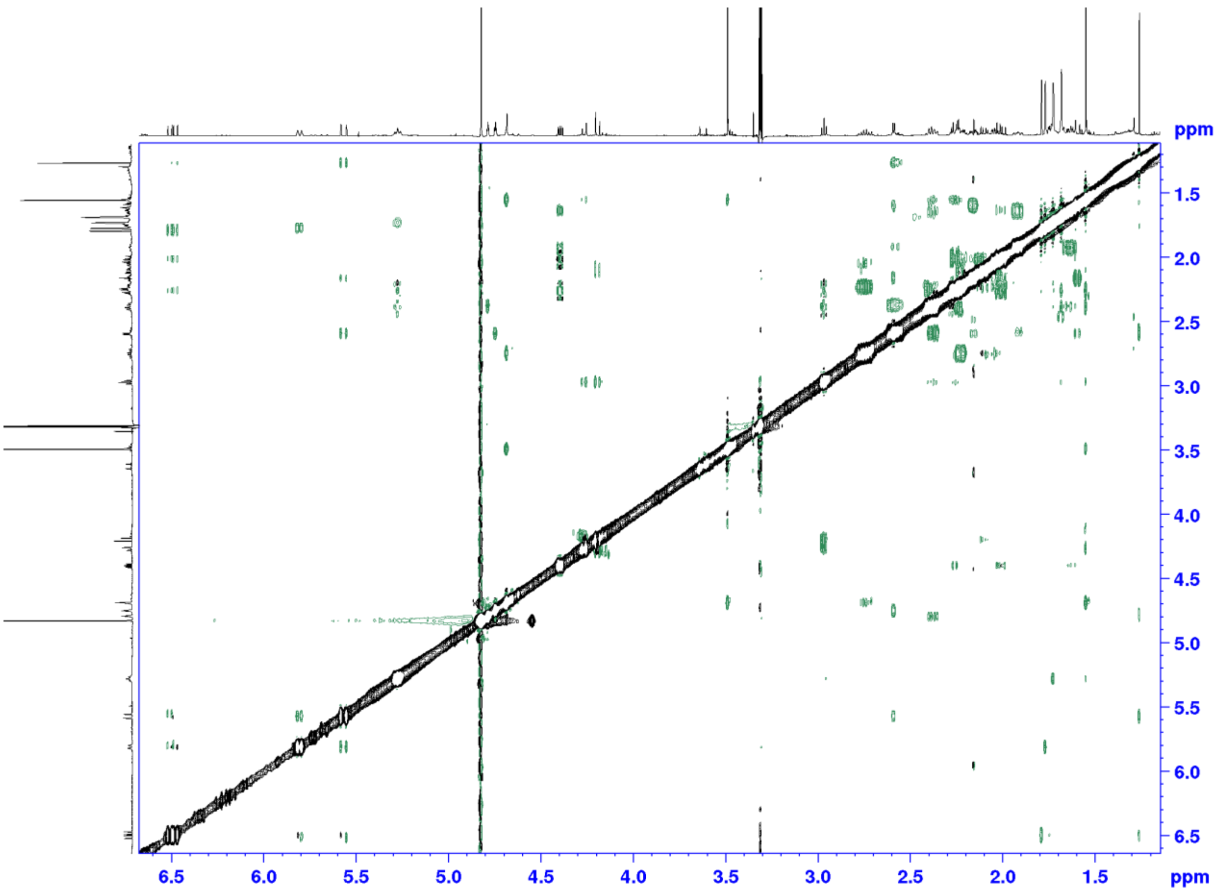


Figure S21. NOESY (500 MHz, CD_3OD) spectrum of pseudallicin B (**4**)

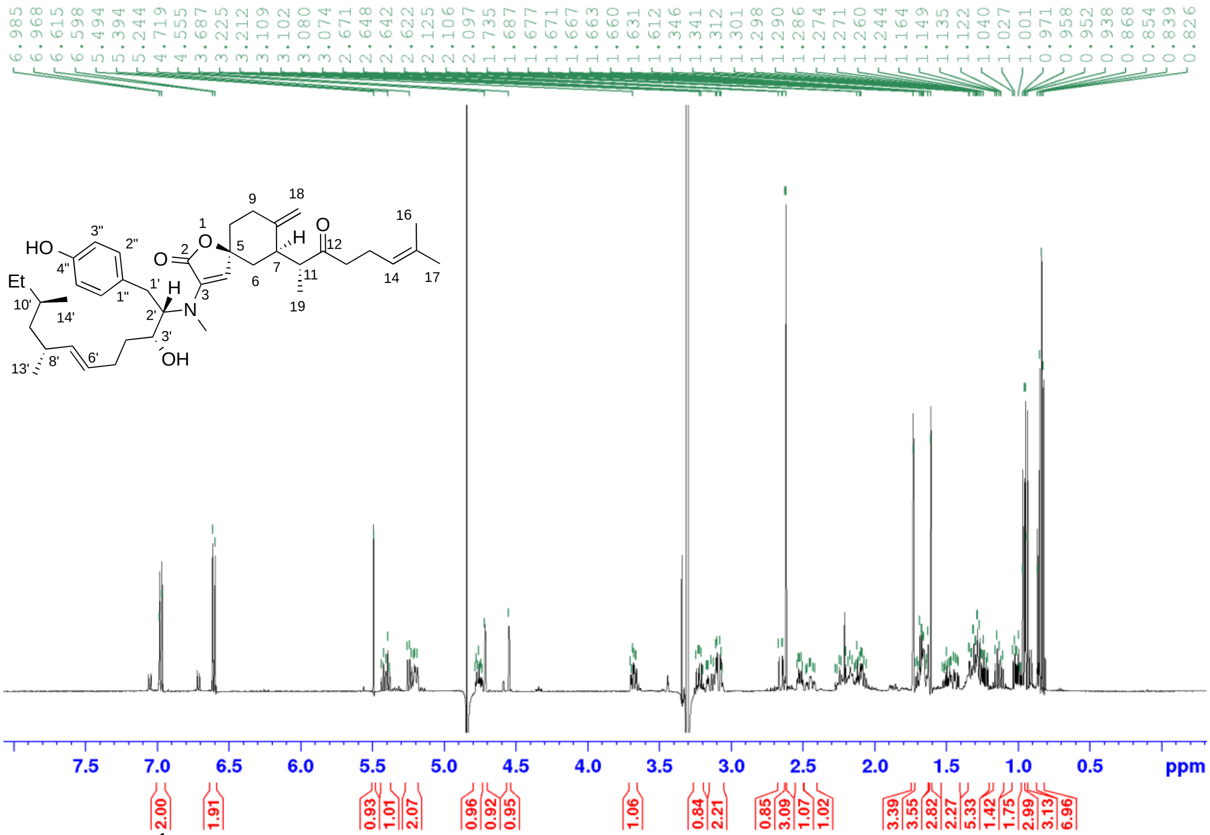


Figure S22. ^1H (500 MHz, CD_3OD) spectrum of pseudallicin C (**5**)

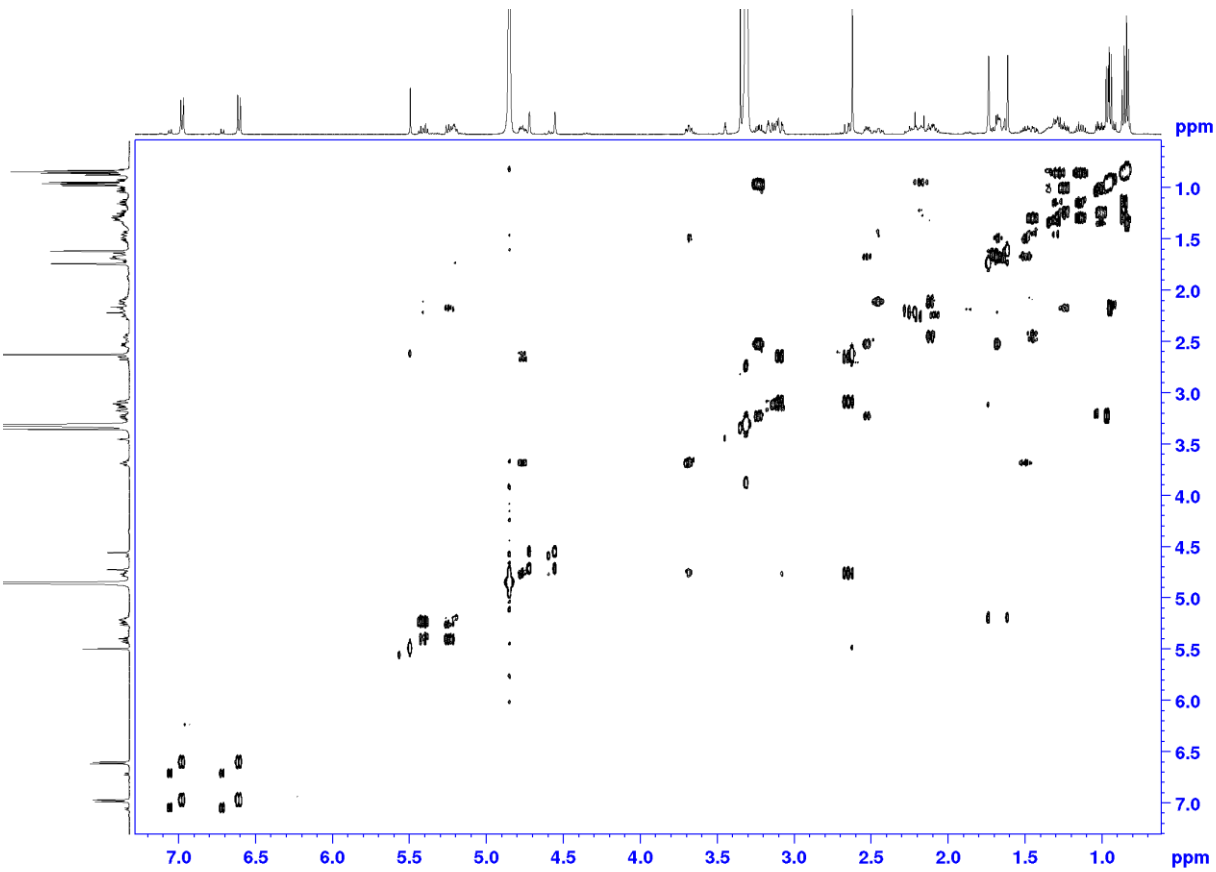


Figure S23. COSY (500 MHz, CD_3OD) spectrum of pseudallicin C (**5**)

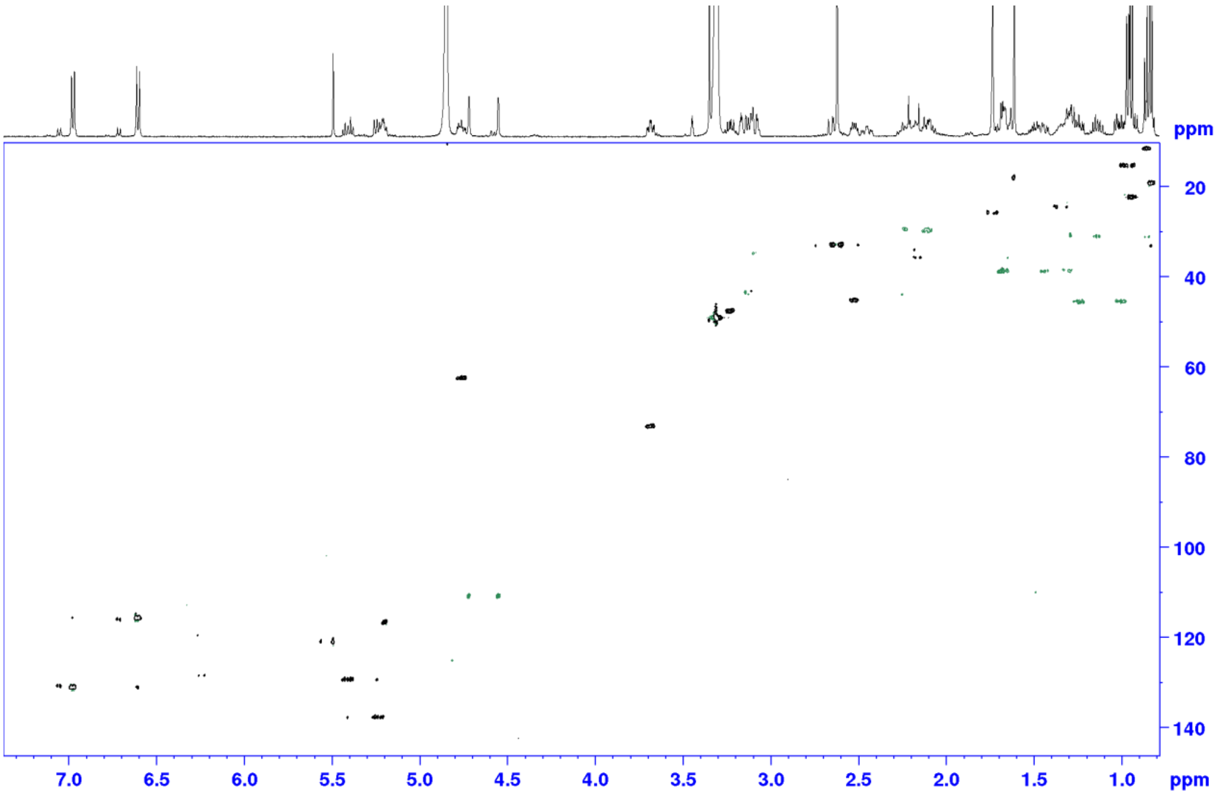


Figure S24. HSQC spectrum of pseudallicin C (**5**) in CD_3OD

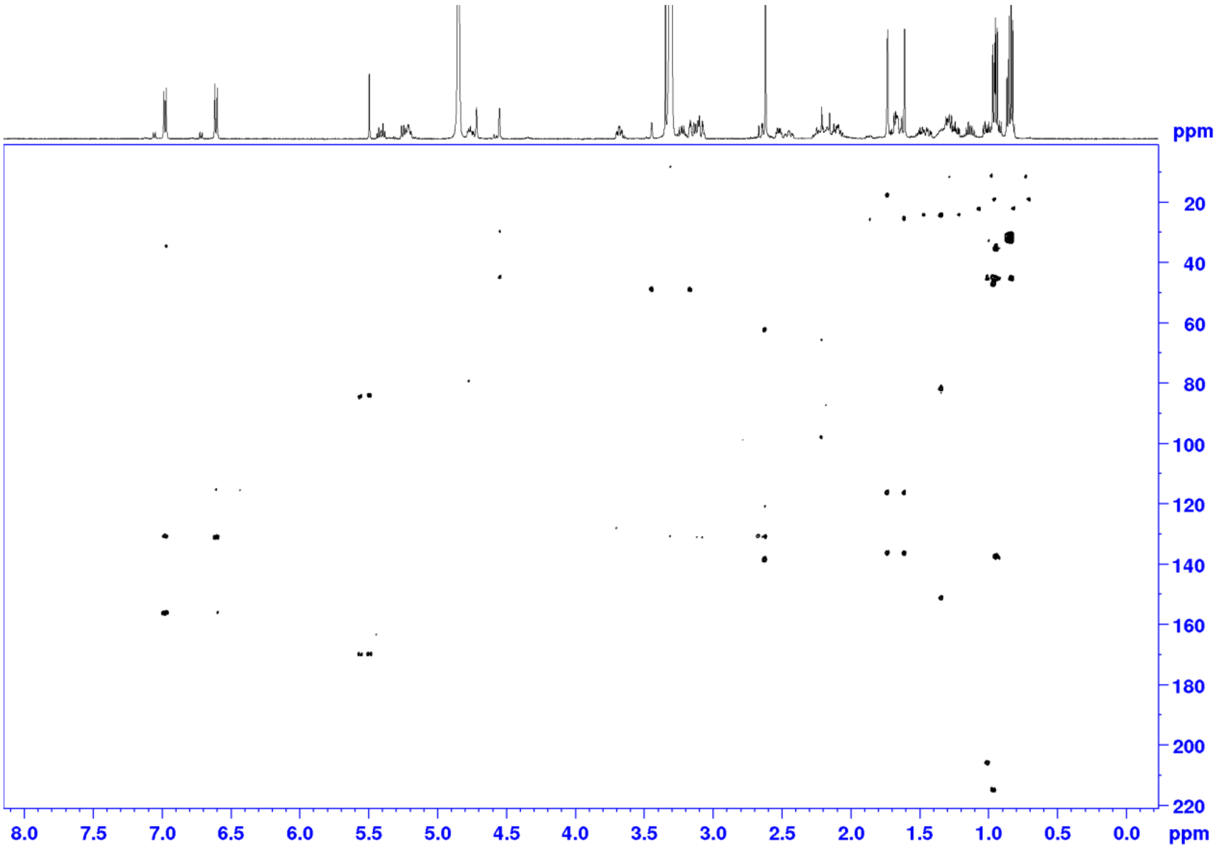


Figure S25. HMBC spectrum of pseudallicin C (**5**) in CD_3OD

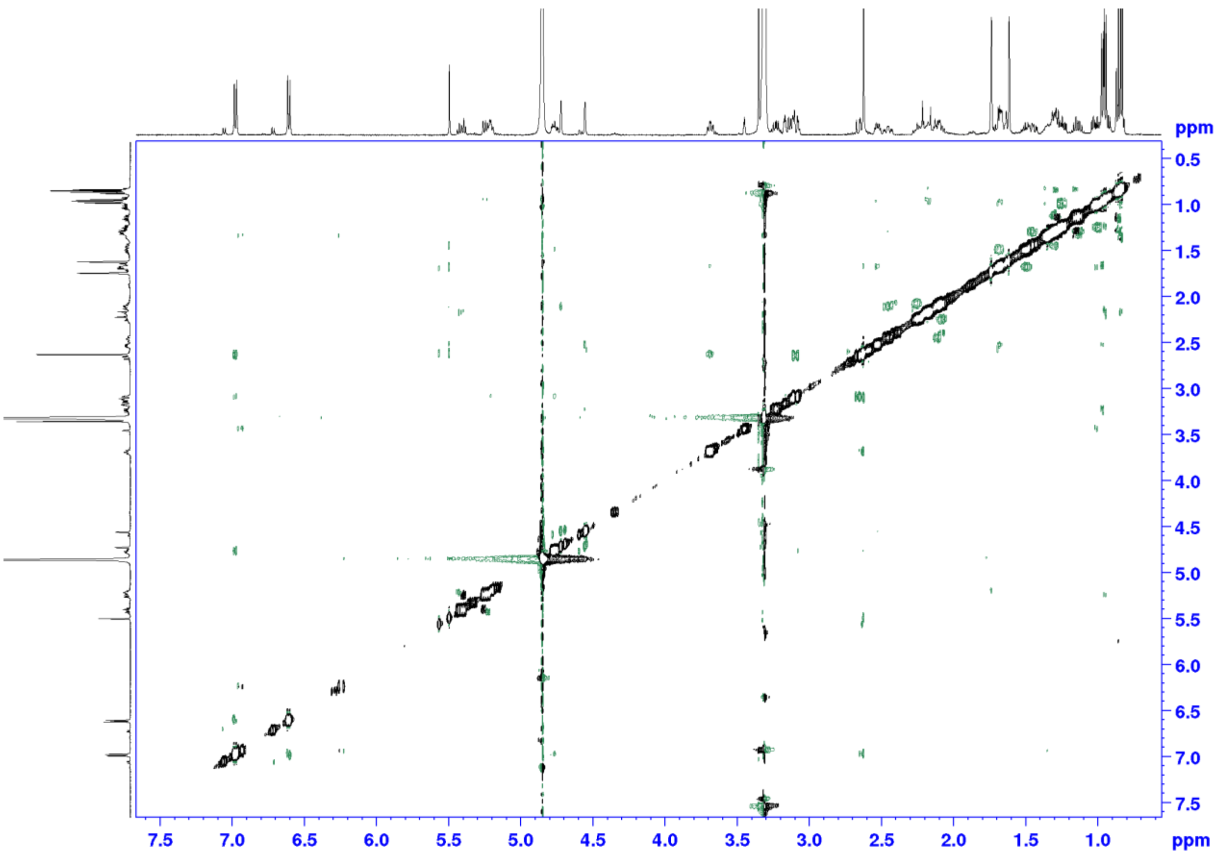


Figure S26. NOESY (500 MHz, CD_3OD) spectrum of pseudallicin C (**5**)

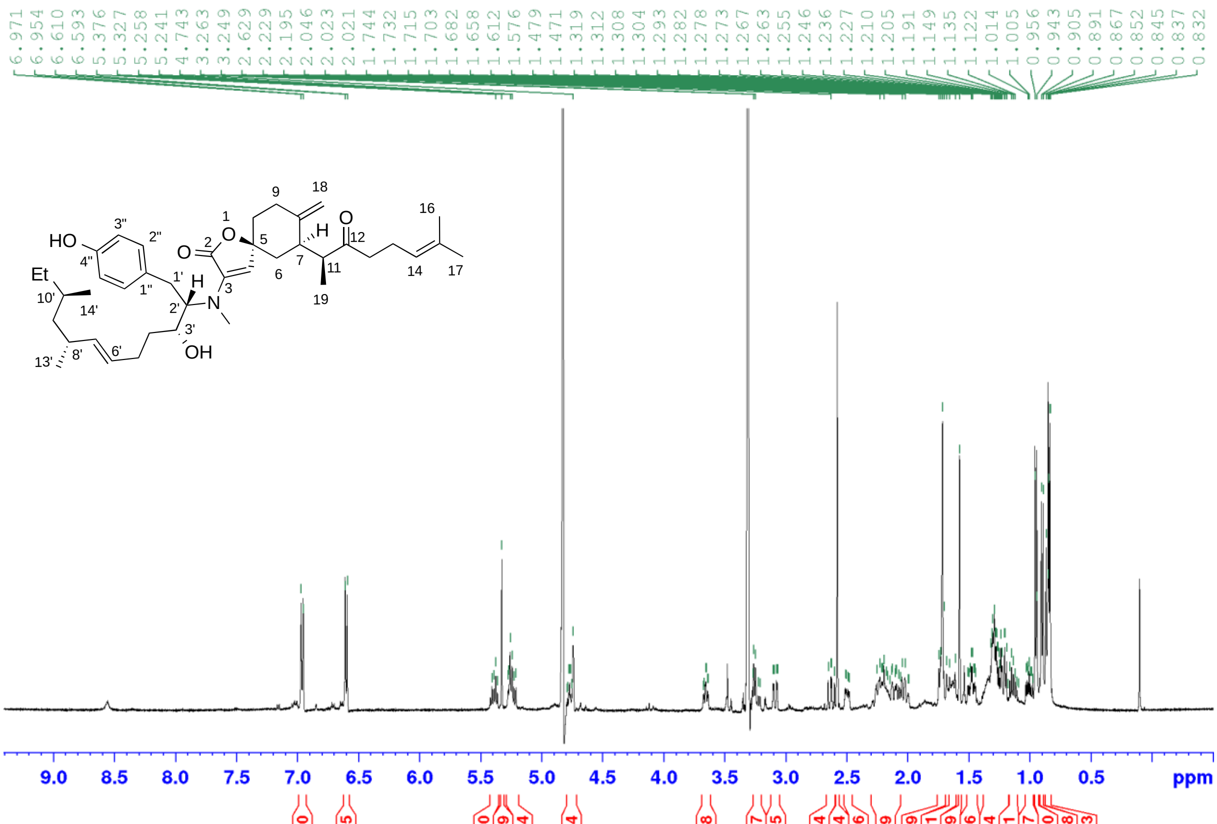


Figure S27. ^{1}H (500 MHz, CD_3OD) spectrum of pseudallicin D (**6**)

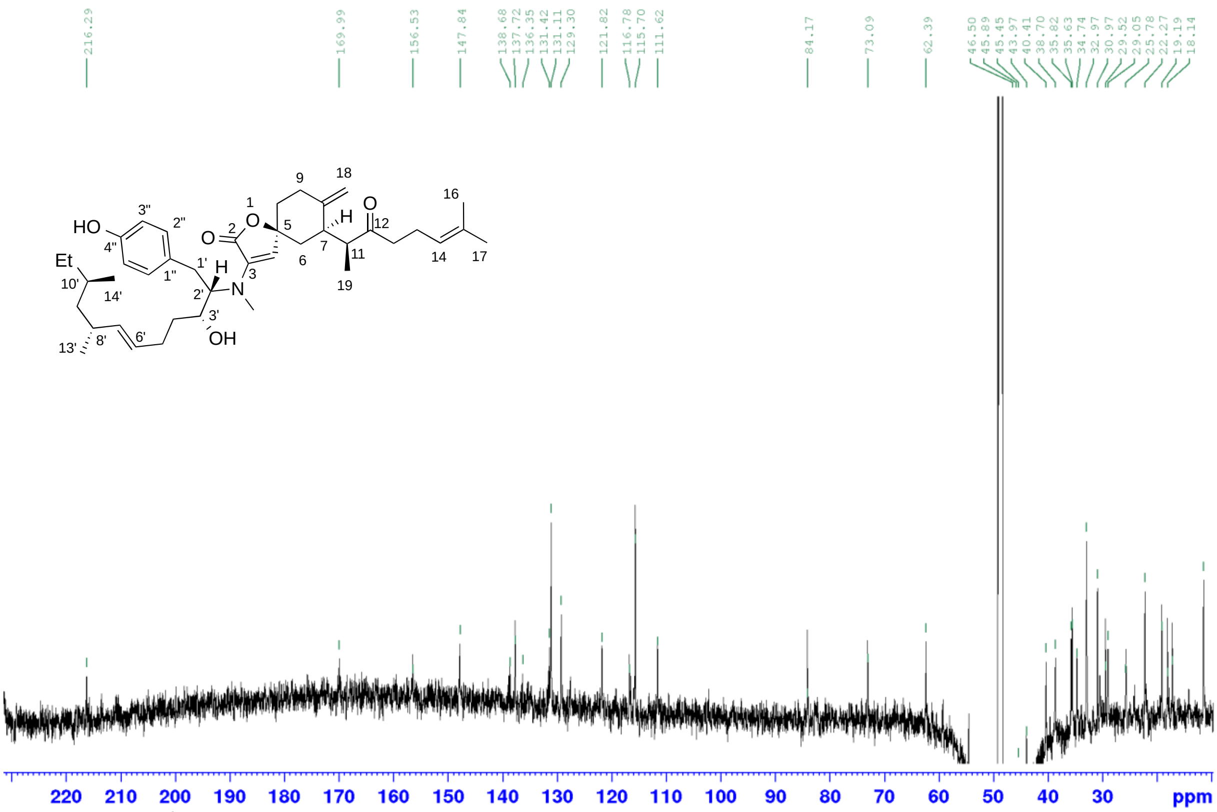


Figure S28. ^{13}C (150 MHz, CD_3OD) spectrum of pseudallicin D (**6**)

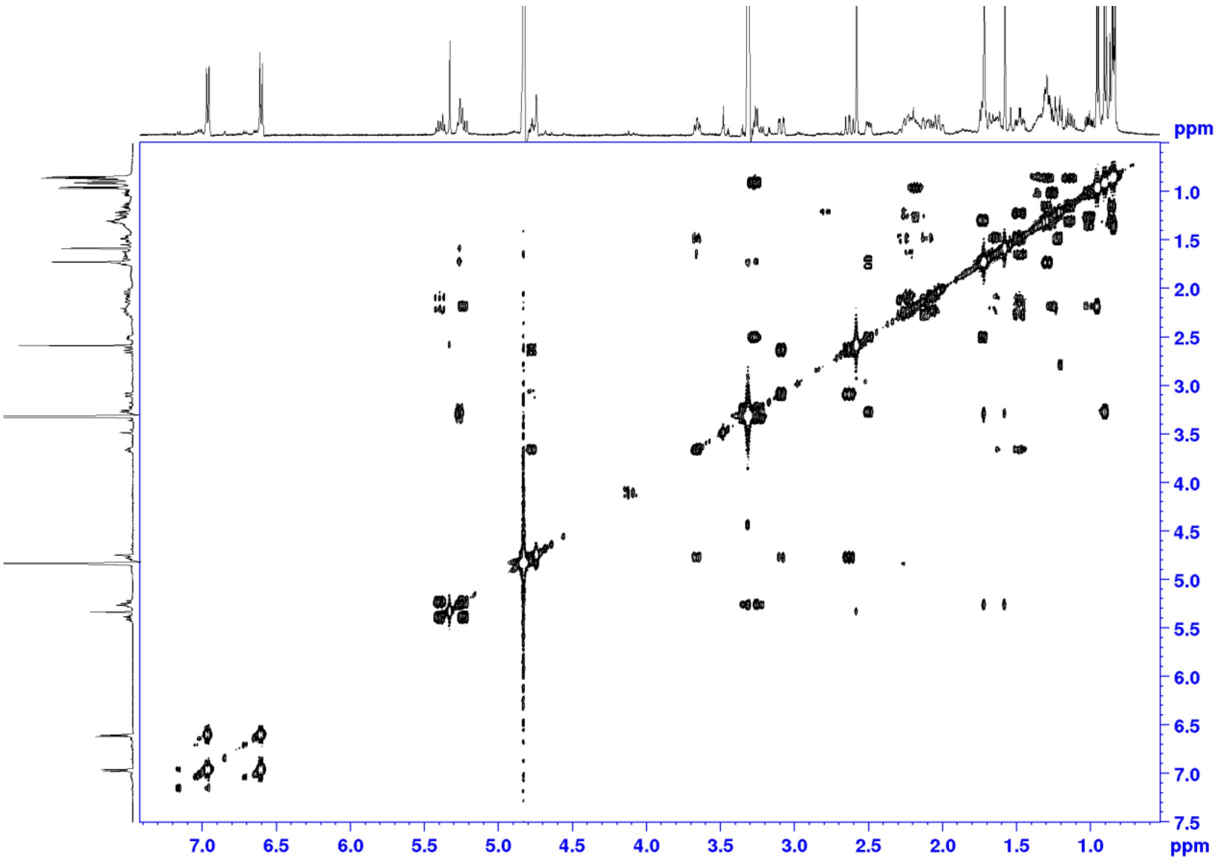


Figure S29. COSY (500 MHz, CD_3OD) spectrum of pseudallicin D (**6**)

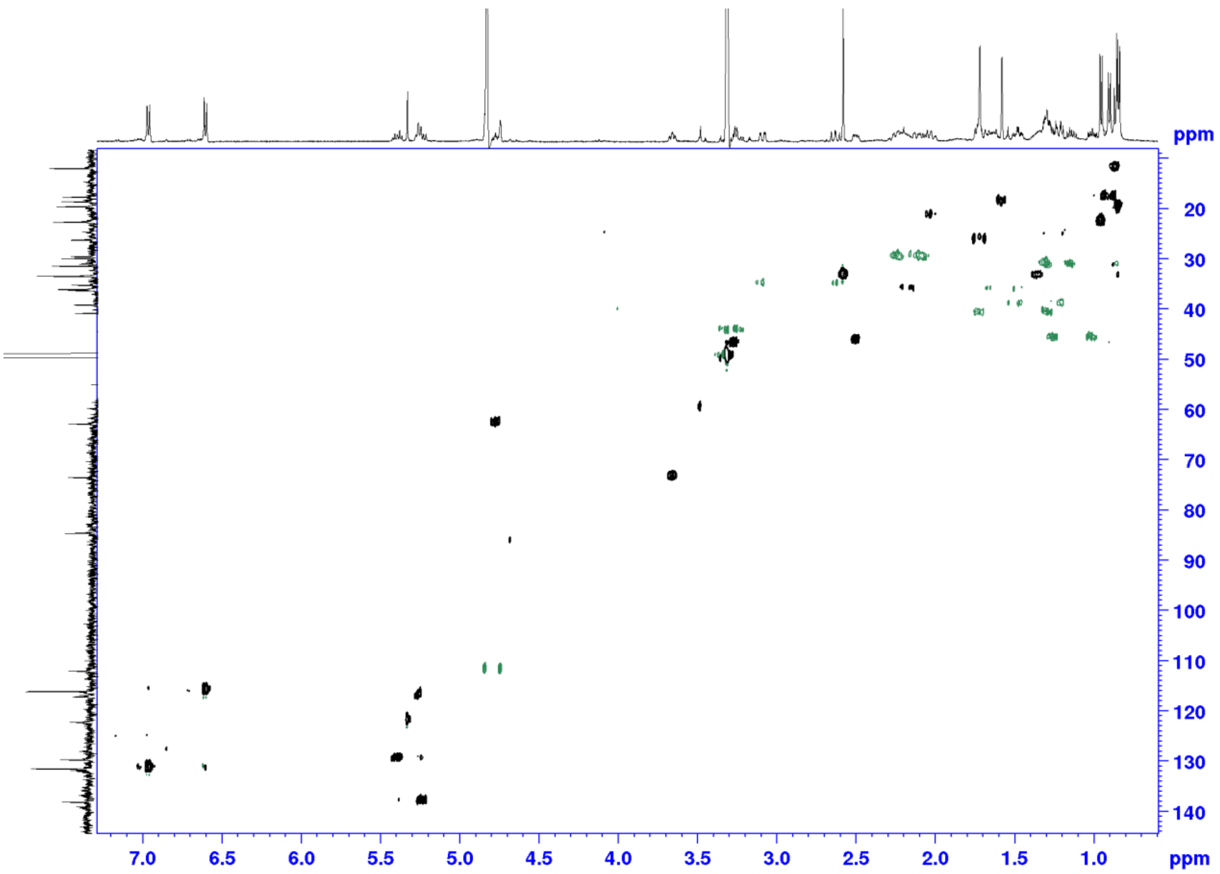


Figure S30. HSQC spectrum of pseudallicin D (**6**) in CD_3OD

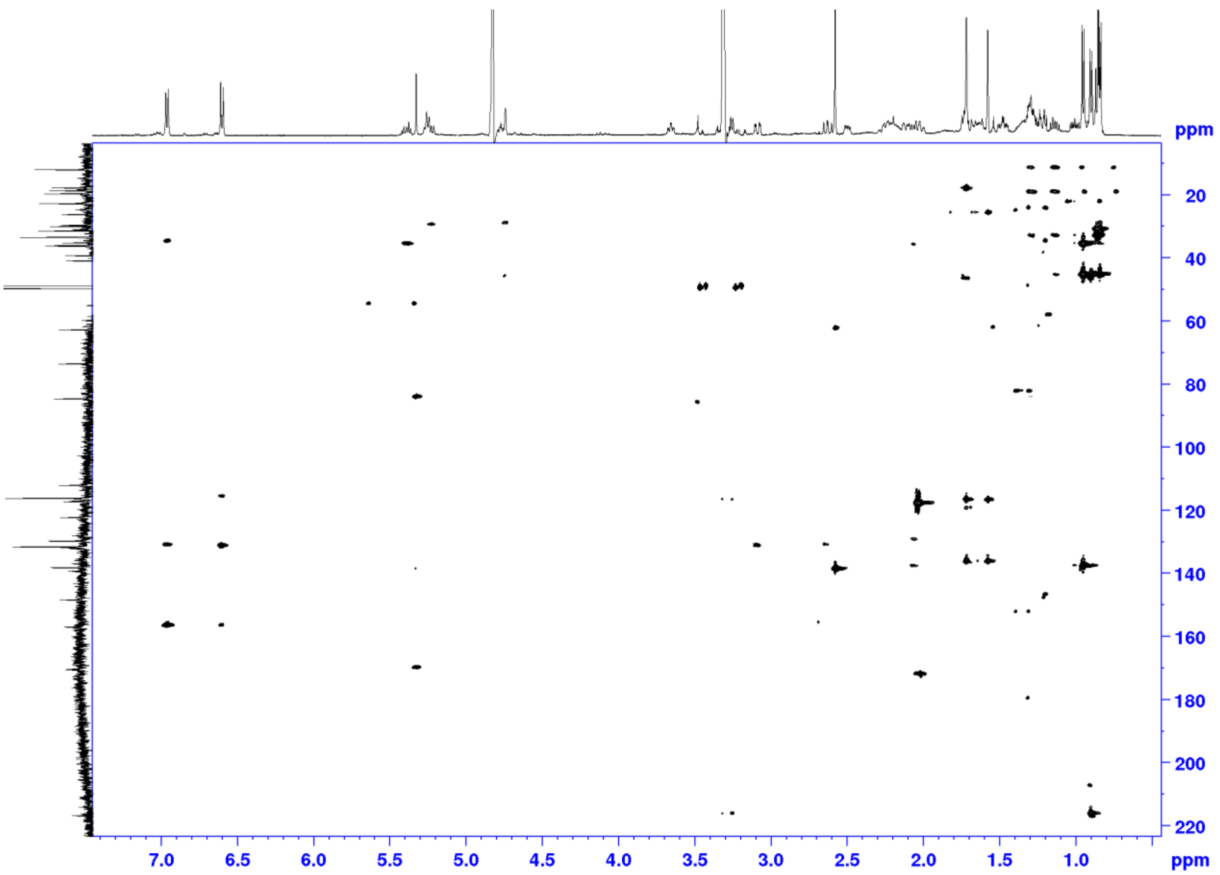


Figure S31. HMBC spectrum of pseudallicin D (**6**) in CD_3OD

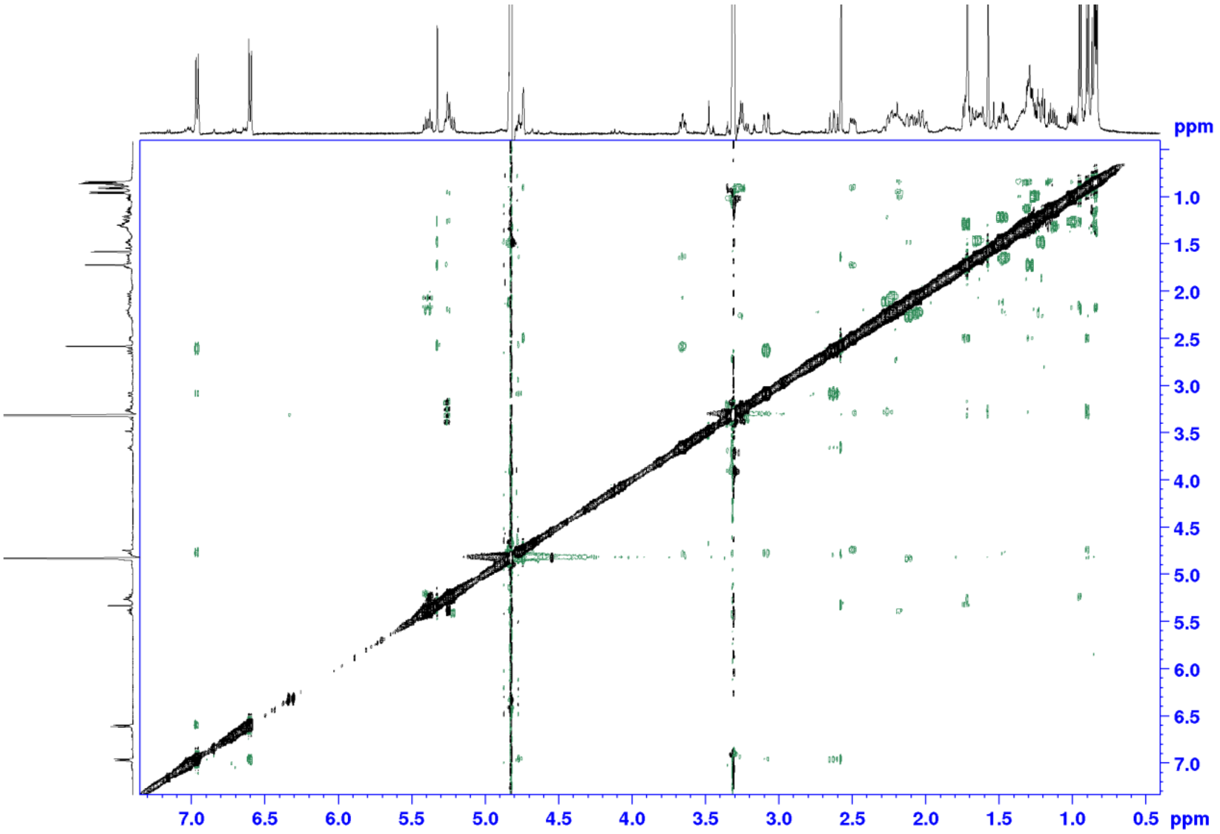


Figure S32. NOESY (500 MHz, CD_3OD) spectrum of pseudallicin D (**6**)

REFERENCES

(1) Takamatsu, S.; Kim, Y.-P.; Komiya, T.; Sunazuka, T.; Hayashi, M.; Tanaka, H.; Komiyama, K.; Omura, S. *J. Antibiotics* **1996**, *49*, 635.

(2) Zhang, P.; Bao, Q.; Dang, H. T.; Hong, J.; Lee, H. J.; Yoo, E. S.; Bae, K. S.; Jung, J. H. *J. Nat. Prod.* **2009**, *72*, 270.

(3) Lin, H.; Tsunematsu, Y.; Dhingra, S.; Xu, W.; Fukutomi, M.; Chooi, Y.; Cane, D. E.; Calvo, A. M.; Watanabe, K.; Tang, Y. *J. Am. Chem. Soc.* **2014**, *136*, 4426.

(4) Nirma, C.; Eparvier, V.; Stien, D. *J. Nat. Prod.* **2013**, *76*, 988.